Environmental Chemistry for a Sustainable World 27

Nandita Dasgupta
Shivendu Ranjan
Eric Lichtfouse *Editors*

Environmental Nanotechnology Volume 3

Springer

Environmental Chemistry for a Sustainable World

Volume 27

Other Publications by the Editors

Books
Environmental Chemistry
http://www.springer.com/978-3-540-22860-8

Organic Contaminants in Riverine and Groundwater Systems
http://www.springer.com/978-3-540-31169-0

Sustainable Agriculture
Volume 1: http://www.springer.com/978-90-481-2665-1
Volume 2: http://www.springer.com/978-94-007-0393-3

Book series
Environmental Chemistry for a Sustainable World
http://www.springer.com/series/11480

Sustainable Agriculture Reviews
http://www.springer.com/series/8380

Journals
Environmental Chemistry Letters
http://www.springer.com/10311

More information about this series at http://www.springer.com/series/11480

Nandita Dasgupta • Shivendu Ranjan
Eric Lichtfouse
Editors

Environmental Nanotechnology
Volume 3

Springer

Editors
Nandita Dasgupta
Department of Biotechnology
Institute of Engineering and Technology
Lucknow, Uttar Pradesh, India

Eric Lichtfouse
Aix Marseille University, CNRS, IRD
INRA, Coll France, CEREGE
Aix-en-Provence, France

Shivendu Ranjan
Centre for Technological Innovations &
Industrial Research (CTIIP)
South Asian Institute for Advanced Research
and Development (SAIARD)
Kolkata, India

ISSN 2213-7114 ISSN 2213-7122 (electronic)
Environmental Chemistry for a Sustainable World
ISBN 978-3-030-26671-4 ISBN 978-3-030-26672-1 (eBook)
https://doi.org/10.1007/978-3-030-26672-1

© Springer Nature Switzerland AG 2020
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG.
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

We dedicate this book to those who are affected by environmental hazards. We hope that this book may be a small contribution to improving their quality of life.

Think Environment – Think Nanomaterials
- Dr. Nandita Dasgupta

This book is the third volume of *Environmental Nanotechnology* from its several volumes and contains the chapters related to nanoremediation, waste water purification, nanosensors, nanomedicine, and nanofiltration. This book also highlights the safety aspects and risk assessment and management related to several toxins and nanotechnology-related solution for these challenges. New nanomaterials have been discussed from the nexus of environment, water, remediation, and total environment. Total environment is a main factor issue to decide good health of human mankind as well as for food and agriculture in the context of health, sustainable growth, and efficient agro-food product development. As a consequence, novel technologies are emerging fast, and environmental nanotechnology is one among them. In particular, pollution issues of air and water can be solved by environmental nanotechnologists, which include nanobioremediation, nanonutraceuticals, nanobiosensors, and nanodegradation.

The first chapter by Agboola et al. discusses about the nanomaterials for sustainable environment and clean water. Then, Lupu et al. review the use of inorganic nanomaterials in therapeutic applications of malignant diseases in Chap. 2. In Chap. 3, Klosov and Klosova et al. explain the modification of oligomers and reinforced polymeric composites by carbon nanotubes and ultrasonic. Interaction of nanomaterials with soil is reviewed in Chap. 4 by Piplai et al. Applications of nanotechnology for water treatment are presented by Ali and Ahmad in Chap. 5. Overview of nanomaterial-assisted technologies for denitrification processes has been presented by Mirbagheri and coauthors in Chap. 6. Lohith et al. detail the nanoencapsulation of food carotenoids in Chap. 7. Overview on nanomaterials for agricultural applications has been presented by Garg and Payasi in Chap. 8. In Chap. 9, Singh and Kumar present the effect of the interaction of nanoparticles with roots on the uptake in plants. Hassan and Elkady describe the semiconductor nanomaterial applications for gas sensor applications in Chap. 10.

Thanks for reading!

Lucknow, Uttar Pradesh, India Nandita Dasgupta
Kolkata, India Shivendu Ranjan
Aix-en-Provence, France Eric Lichtfouse

Contents

1 Nanotechnology in Wastewater and the Capacity of Nanotechnology for Sustainability 1
Oluranti Agboola, Patricia Popoola, Rotimi Sadiku, Samuel Eshorame Sanni, Sunday Ojo Fayomi, and Olawale Samuel Fatoba

2 Therapeutic Use of Inorganic Nanomaterials in Malignant Diseases 47
Andreea-Roxana Lupu, Traian Popescu, and Marko Stojanović

3 Modification of Oligomers and Reinforced Polymeric Composites by Carbon Nanotubes and Ultrasonic 89
Aleksandr Evhenovych Kolosov and Elena Petryvna Kolosova

4 Understanding Interactions of Nanomaterials with Soil: Issues and Challenges Ahead 117
Tropita Piplai, Tanushree Parsai, Arun Kumar, and Babu J. Alappat

5 Nanotechnology for Water Treatment 143
Zarshad Ali and Rashid Ahmad

6 Overview of Nanomaterial-Assisted Technologies for Denitrification Processes 165
Naghmeh Sadat Mirbagheri, Samad Sabbaghi, Pu Chen, and Zahra Bahmani

7 Nanoencapsulation of Food Carotenoids 203
D. H. Lohith Kumar, Jayeeta Mitra, and S. S. Roopa

8 Nanomaterials in Agricultural Research: An Overview 243
Deepa Garg and Devendra K. Payasi

9 Understanding the Effect of the Interaction of Nanoparticles with Roots on the Uptake in Plants . . . 277
Divya Singh and Arun Kumar

10 Semiconductor Nanomaterials for Gas Sensor Applications . . . 305
Hassan Shokry Hassan and Marwa Farouk Elkady

Index . . . 357

About the Editors

Nandita Dasgupta has completed her BTech and PhD from VIT University, Vellore, India. She is Elected Fellow (FBSS) of Bose Science Society. She has major working experience in micro-/nanoscience and is currently working as Assistant Professor at the Department of Biotechnology, Institute of Engineering and Technology, Lucknow, India. Earlier at LV Prasad Eye Institute, Bhubaneswar, India, she has worked on mesenchymal stem cell-derived exosomes for the treatment of uveitis. She has exposure of working at university, research institutes, and industries including VIT University, Vellore, Tamil Nadu, India; CSIR-Central Food Technological Research Institute, Mysore, India; Uttar Pradesh Drugs & Pharmaceutical Co. Ltd., Lucknow, India; and Indian Institute of Food Processing Technology (IIFPT), Thanjavur, Ministry of Food Processing Industries, Government of India. At IIFPT, Thanjavur, she was involved in a project funded by a leading pharmaceutical company, Dr. Reddy's Laboratories, and has successfully engineered micro-vehicles for model drug molecules. Her areas of interest include micro/nanomaterial fabrication and its applications in various fields – medicine, food, environment, agriculture and biomedicine.

She has published 13 edited books and 1 authored book with Springer, Switzerland. She is an Associate Editor of *Environmental Chemistry Letters* – a Springer journal with an impact factor of 3.2.

Shivendu Ranjan has completed his BTech and PhD in Biotechnology from VIT University, Vellore, India, and has expertise in nano(bio)technology. He is Elected Fellow of Bose Science Society (FBSS) and is currently working as Head of Research & Technology Development at E-Spin Nanotech Pvt. Ltd., SIDBI Center, Indian Institute of Technology, Kanpur, India. After joining E-Spin Nanotech, IIT, Kanpur, he has successfully developed prototypes for many products and three patents. He is also serving as a Senior Research Associate (Adjunct) at the Faculty of Engineering and Built Environment, University of Johannesburg, Johannesburg, South Africa. He is also mentoring Atal Innovation Centre, Bhubaneswar, Odisha, and giving his technical inputs to the center. Atal Innovation Centre is the part of Atal Innovation Mission of the NITI Aayog, Government of India. He is also Reviewer of Iran National Science Foundation (INSF), Tehran, Iran, and Jury at Venture Cup, Denmark, from the past three consecutive years. He had founded and drafted the concept for the first edition of the "VIT Bio Summit" in 2012, and the same has been continued till date by the university. He has worked in CSIR-CFTRI, Mysuru, India, as well as in UP Drugs and Pharmaceutical Co. Ltd., India, and IIFPT, Thanjavur, MoFPI, Government of India. At IIFPT, Thanjavur, he was involved in a project funded by a leading pharmaceutical company, Dr. Reddy's Laboratories, and has successfully engineered micro-vehicles for model drug molecules.

His research interests are multidisciplinary which includes micro-/nanobiotechnology, nano-toxicology, environmental nanotechnology, nanomedicine, and nanoemulsions. He is an Associate Editor of *Environmental Chemistry Letters* – a Springer journal with an impact factor of 3.2. He has published six edited books and one authored book with Springer, Switzerland, and many scientific articles in international peer-reviewed journals, and has authored many book chapters as well as review articles. He has also received several awards and recognitions from different national and international organizations.

Eric Lichtfouse PhD, born in 1960, is an Environmental Chemist working at the University of Aix-Marseille, France. He has invented carbon-13 dating. He is teaching scientific writing and communication and has published the book *Scientific Writing for Impact Factor Journals*, which includes a new tool – the micro article – to identify the novelty of research results. He is Founder and Chief Editor of scientific journals and series in environmental chemistry and agriculture. He founded the European Association of Chemistry and the Environment. He received the Analytical Chemistry Prize by the French Chemical Society, the Grand Prize of the Universities of Nancy and Metz, and a Journal Citation Award by the Essential Indicators.

Contributors

Oluranti Agboola Department of Chemical Engineering, Covenant University, Ota, Nigeria
Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa

Rashid Ahmad Department of Chemistry, University of Malakand, Chakdara, Pakistan

Babu J. Alappat Professor, Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India

Zarshad Ali Department of Chemistry, Hazara University, Mansehra, Pakistan

Zahra Bahmani Nanochemical Engineering Department, Faculty of Advanced Technologies, Shiraz University, Shiraz, Iran

Pu Chen Department of Chemical Engineering, University of Waterloo, Waterloo, ON, Canada

Marwa Farouk Elkady Chemical and Petrochemical Engineering Department, Egypt-Japan University for Science and Technology, New Borg El-Arab City, Alexandria, Egypt
Fabrication Technology Researches Department, Advanced Technology and New Materials and Research Institute, City of Scientific Research and Technological Applications, Alexandria, Egypt

Olawale Samuel Fatoba Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa

Sunday Ojo Fayomi Department of Chemical Engineering, Covenant University, Ota, Nigeria
Department of Mechanical Engineering, Covenant University, Ota, Nigeria

Deepa Garg Department of Biotechnology, Kurukshetra University, Kurukshetra, Haryana, India

Hassan Shokry Hassan Electronic Materials Researches Department, Advanced Technology and New Materials Researches Institute, City of Scientific Researches and Technological Applications, New Borg El-Arab City, Alexandria, Egypt
Physics Department, Faculty of Science, Aljouf University, Aljouf, Saudi Arabia

Elena Petryvna Kolosova Physics and Mathematics Faculty, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine

Aleksandr Evhenovych Kolosov Chemical, Polymeric and Silicate Machine Building Department of Chemical Engineering Faculty, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine

Arun Kumar Associate Professor, Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India

D. H. Lohith Kumar Bioprocess Engineering Laboratory, Department of Biotechnology, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand, India

Andreea-Roxana Lupu Immunology Laboratory, "Cantacuzino" National Medico – Military Institute for Research and Development, Bucharest, Romania
Immunobiology Laboratory, Assay Development and Alternative Studies Department, "Victor Babes" National Research Institute of Pathology, Bucharest, Romania

Naghmeh Sadat Mirbagheri Nanochemical Engineering Department, Faculty of Advanced Technologies, Shiraz University, Shiraz, Iran

Jayeeta Mitra Department of Agricultural and Food Engineering, Indian Institute of Technology, Kharagpur, West Bengal, India

Tanushree Parsai Graduate Student, Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India

Devendra K. Payasi Jawaharlal Nehru Krishi Vishwa Vidyalaya, Regional Agricultural Research Station, Sagar, Madhya Pradesh, India

Tropita Piplai Graduate Student, Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India

Traian Popescu Laboratory of Atomic Structure and Defects in Advanced Materials, National Institute of Materials Physics, Magurele, Romania

Patricia Popoola Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa

S. S. Roopa Britannia Industries Limited, Ramanagara, Karnataka, India

Samad Sabbaghi Nanochemical Engineering Department, Faculty of Advanced Technologies, Shiraz University, Shiraz, Iran
Department of Chemical Engineering, University of Waterloo, Waterloo, ON, Canada

Rotimi Sadiku Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa

Samuel Eshorame Sanni Department of Chemical Engineering, Covenant University, Ota, Nigeria

Divya Singh Department of Civil Engineering, Indian Institute of Technology, New Delhi, India

Marko Stojanović Department of Pharmacology, Clinical Pharmacology and Toxicology, Faculty of Medicine, University of Belgrade, Belgrade, Serbia

Chapter 1
Nanotechnology in Wastewater and the Capacity of Nanotechnology for Sustainability

**Oluranti Agboola, Patricia Popoola, Rotimi Sadiku,
Samuel Eshorame Sanni, Sunday Ojo Fayomi, and Olawale Samuel Fatoba**

Contents

1.1 Introduction 2
1.1.1 Green Nanotechnology 3
1.2 Wastewater Treatment Sustainability 4
1.3 Nanotechnology and Water Treatment 5
1.3.1 Nanotechnology in Water Treatment and Remediation 5
1.4 Nanomembranes 23
1.4.1 Carbon Nanotube Composite Membranes 23
1.4.2 Nanoparticle-Based Membranes 25
1.4.3 Ceramic Membranes 26
1.4.4 Nanofiber Membranes for Water Purification 27
1.5 Patent and the Industries Providing Nanotechnology Products 29
1.5.1 Patents on Nanoparticles for Its Applications in Wastewater Treatment 30
1.5.2 Patents on Nanofibres for Its Applications in Desalination 31
1.5.3 Companies in Collaboration with U.S. Patents 31
1.6 Challenges 32

O. Agboola (✉)
Department of Chemical Engineering, Covenant University, Ota, Nigeria

Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa
e-mail: oluranti.agboola@covenantuniversity.edu.ng

P. Popoola · R. Sadiku · O. S. Fatoba
Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa
e-mail: popoolaapi@tut.ac.za; sadikur@tut.ac.za

S. E. Sanni
Department of Chemical Engineering, Covenant University, Ota, Nigeria
e-mail: samuel.sanni@covenantuniversity.edu.ng

S. O. Fayomi
Department of Chemical Engineering, Covenant University, Ota, Nigeria

Department of Mechanical Engineering, Covenant University, Ota, Nigeria
e-mail: ojo.fayomi@covenantuniversity.edu.ng

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_1

1.7 Conclusions 33
References 34

Abstract About 70% of the Earth's surface is covered with water; unfortunately, there is difficulty in accessing 3% of the water as freshwater that is fit for human consumption. The paucity of safe and universal freshwater is a serious challenge across developed, transition and developing countries due to the globalisation processes and the ever-increasing consumer society. The dynamisms of the rising global demand for freshwater are the growth of the world population, industrial activities, upgrade in standards of living, altering consumption pattern and the increase of agricultural irrigation. Furthermore, climate change, such as pollution at elevated level, change in weather patterns, emission of greenhouse gases, deforestation and uneconomical use of water, are the causes of water paucity. The invariable nature of global water paucity is the geographic and temporal disproportion between the demand for freshwater and the availability of freshwater. The transformation in the development of novel nanomaterials, such as activated carbon, carbon nanotubes, nanoparticles and nanofibres, is among the most stimulating and promising innovative nanotechnologies for wastewater treatment. In this report, we reviewed the use of nanotechnology in wastewater treatment and the capacity of nanotechnology for sustainability. Thus, the major points are as follows: (1) nanotechnology in water treatment and remediation promises to overcome the major obstacles to having clean freshwater, (2) sustainability of using nanotechnology to solve the problem of water paucity of the present generation without compromising the needs of the future generations, (3) the use of nanoadsorption technology with different types of nanoadsorbents in order to provide new treatment capabilities, (4) the use of nanomembranes for water treatment to allow the economic utilisation of unconventional water sources in order to increase safe and clean water supply, (5) patents that carefully utilise nanotechnology innovations and (6) the challenges of using nanotechnology in wastewater treatment.

Keywords Water treatment · Nanotechnology · Nanomaterials · Nanoadsorption · Nano membranes · Nanoparticles · Carbon nanotubes · Nanofibre · Activated carbon · Patents

1.1 Introduction

The provision of safe freshwater supply in an efficient manner is one of the most recent serious global challenges. The challenge constitutes a major threat to water paucity, health and economic growth. Furthermore, the challenge of providing sufficient and safe drinking water is made complicated by climate change and the pressures of economic development and industrialisation. The public and the industrial sectors consume substantial amounts of freshwater while producing vast quantities of wastewater (Tong and Elimelech 2016). If inadequately treated, wastewater discharges into the aquatic environment would cause severe pollution, which would adversely impact on the aquatic ecosystems and public health (Schwarzenbach et al. 2010). Despite of the challenge, freshwater supply is achievable through new technologies. The ultimate goal of any technology should be to improve the environment. Nanotechnology is an interdisciplinary field that strives to manage, produce and develop novel prospect to use science, engineering and new approaches with nanoscale invention to support humans and environmental health (Verma and Tyagi 2016). Nanotechnology deals with dimensions and tolerances of less than 100 nanometres, especially with the manipulation of individual atoms and molecules. Nanotechnology has the capability of manipulating nanoparticles as building blocks for explicit applications, which reflects an improvement in the design and applications of materials and devices that demonstrate new and sustainable future. As a result of the advancement in nanotechnology, different applications in green nanotechnology appear to be new and promising research fields. Thus, the use of nanotechnology is enhanced by green technology (Verma et al. 2017). This chapter reviews the use of green nanotechnology for the treatment of wastewater and the capability of the application of nanotechnology for sustainability. The application of nanomaterials in wastewater treatment, patents that cautiously exploits nanotechnology innovation and the challenges of using nanomaterials in the treatment of wastewater are also reviewed.

1.1.1 Green Nanotechnology

Green nanotechnology is the technology that has been employed for the development of clean technologies. Green technology is based on the principles of green engineering and green chemistry. The concept of green technology seeks to provide medical help, energy, clean water and a good environment in a sustainable manner (Basiuk and Basiuk 2015). Green nanotechnology uses nanomaterials to minimise potential environmental and human health hazards associated with the manufacture and use of nanotechnology products. Green nanotechnology further encourages the replacement of existing products with new nano products that are more environmentally friendly throughout nano product lifecycle. The development of nanomaterials involves several key steps. Two most important steps are: the synthesis of size and shape of controlled nanoparticles is the first key in developing nanomaterials. Secondly, characterisation of nanoparticles is indispensable in order to understand the behaviour and properties of nanoparticles, aiming at implementing nanotechnology. Furthermore, characterisation of nanoparticles aims at controlling nanoparticle behaviour and designing new material systems with super performance (Sadiku and Sadiku 2010).

The awareness on the behaviour of nanomaterials and the new developments in nanotechnology have undoubtedly shown the advantages of using a high surface-to-mass ratio in heterogeneous reactions. Additionally, the tremendous capabilities of very small materials that are suitable to act at the molecular scale have been discovered (de la Guardia 2014). Green technology gives emphasis on the use of nanotechnology in order to uplift the environmental sustainability of processes that are currently exhibiting negative effects. In addition, fabricating green products and use them in support of sustainability will primarily help in reducing human health and likely environmental risks (Thangavel and Sridevi 2015). This is applicable in two different magnitudes. The first magnitude includes producing nanomaterials and nanoproducts that can help in minimising harm to human health or the environment (Karn and Bergeson 2009). The second magnitude includes making green nanoproducts and using them to support sustainability by giving solutions to environmental difficulties. These green nanoproducts are used to prevent harm from pollutants and are incorporated into environmental technologies to remediate hazardous waste site, clean up pollutant streams and desalinate water among other applications (Hashem 2014).

1.2 Wastewater Treatment Sustainability

The continuous disposal of waste and wastewater to the environment by consumers, municipalities and industries, as well as agricultural liquid, solid and gaseous wastes constitutes one of the most critical threats to the sustainability of human civilisation. This undesirable behaviour contaminates the water, land and air, thus, contributing to global warming. With increasing population and economic growth, the treatment and safe disposal of wastewater is very important in order to preserve public health and minimise unbearable levels of environmental degradation. Furthermore, efficient wastewater management is very essential in order to prevent water bodies from being contaminated for the purpose of preserving the sources of clean water (Jhansi et al. 2013). Sustainability aspires for the preservation of public and economic wellbeing. Sustainability also aspires for the protection of the environment and the judicious use of natural resources and equitable social progress, which recognises the just requirements of all individuals, communities and the environment (Muga and Mihelcic 2008). The new challenge of wastewater treatment is to shift the standard from a toxic polluted water to a viable resource in the context of wastewater treatment sustainability development. Sustainability in the context of wastewater treatment can be defined as solving the problem of water paucity of the present generation without compromising the needs of the future generations. Thus, sustainability is the key for the reduction and prevention of the adverse effects of environmental issues (Thangavel and Sridevi 2015). Sustainability of wastewater treatment systems can be assessed through different assessment tools, such as exergy analysis, economic analysis, life-cycle assessment and the use of green nanotechnology (Muga and Mihelcic 2008). The next section discusses the different uses of green nanotechnology for the treatment of wastewater.

1.3 Nanotechnology and Water Treatment

Obtaining safe drinking water has been a major scope for nanotechnology research and development. Nanotechnologies are a part of a new industrial platform with the capability of surpassing the existing technology-intensive systems for water treatment (Olvera et al. 2017). These technologies refer to a broad range of tools, techniques and applications that involve the uses of particles on the estimated size scale of a few nanometres to hundreds of nanometres in diameter. Particles of this size have some exceptional physiochemical and surface properties that advance themselves to different uses that enable them to contribute to the solutions of the global water problem. Nanotechnology-based solutions for a water deficiency issue include water treatment, desalination and reuse of wastewater (Hashem 2014). The inherent possible aspect of nanotechnology in water applications are divided into three basic parts, viz., water treatment and remediation, sensing and detection, and pollution prevention. Nanotechnology has the potential to positively impact on water quality in the following aspects: water treatment and remediation with easy access and sustainability of water resources through the use of advanced filtration materials that enable greater water reuse, recycling and desalinisation. With respect to sensing and detection, there is a great interest in the development of new and improved sensors for the detection of biological and chemical contaminants at very low concentration in water levels. This section will only focus on nanotechnology for water treatment, remediation, sensing and detection.

1.3.1 Nanotechnology in Water Treatment and Remediation

Among the most exciting and promising pursuits in the area of nanotechnology for water treatment is the innovations and developments of novel technologies that employ nanomaterials to desalinate water. The advancement of nanoscience and nanotechnology has recently shown remarkable potential for the remediation of environmental problems (Sadegh et al. 2014). Some of these advancements employ the smoothly scalable size-dependent properties of nanomaterials that relate to the high specific surface areas, such as fast dissolution, high reactivity and strong sorption. Others make use of the nanomaterial discontinuous properties such as super paramagnetism, localised surface plasmon resonance and quantum confinement effect (Rakhi et al. 2016). When compared to conventional materials, nanomaterial adsorbents have shown significantly higher efficiency and faster removal rate of pollutants from wastewater (Rickerby and Morrison 2007). A variety of efficient, cost-effective and eco-friendly nanomaterials with distinctive functionalities have been developed for possible application in the detoxification of industrial effluents, groundwater, surface water and drinking water (Theron et al. 2008). Water treatment usually involves the adsorption and/or photocatalysis of contaminants and contaminant reduction by nanoparticles and bioremediation. Remediation is the process of pollutant transformation from toxic to less toxic in water and soil (Ghasemzadeh et al. 2014). Hence, the remediation solution should be such that it embraces the best practice.

Nanoadsorption Technology

Adsorption technology is a fast, inexpensive and universal technology used in wastewater treatment. Adsorption is a surface phenomenon that is usually used as a polishing step to remove organic and inorganic contaminants in water and wastewater treatments. When a solution containing adsorbable solute is brought into contact with solids that have highly porous surface, liquid-solid intermolecular forces of attraction cause some of the concentrated solute molecules from the solution to be deposited on the solid surface of the adsorbent. The solute retained (on the solid surface) in adsorption processes is called adsorbate, and the solid on which the adsorbate is retained is called an adsorbent. This surface accumulation of adsorbate on an adsorbent is called adsorption (Rasheed 2013). An adsorption terminology is illustrated in Fig. 1.1. The basis of separation by adsorption technology comes from the formation of an adsorbed phase that has a composition different from that of the bulk fluid phase. By changing the properties of the liquid phase (e.g. concentration, temperature and pH), adsorbed species can be released from the surface and transported back into the liquid phase. Since adsorption is a surface process, key quality parameter of adsorbents is the surface area.

Engineered adsorbents are typically highly porous materials, with surface areas in the range between 10^2 and 10^3 m^2/g. The porosity of engineered adsorbents allows the realisation of such large surfaces as internal surfaces constituted by the pore walls. In contrast, the external surface is typically below 1 m^2/g and therefore of minor relevance (Worch 2012). The progress time of the adsorption process is known as adsorption kinetics. The rate of adsorption is generally restricted by diffusion processes near the external adsorbent surface and within the porous adsorbent particles. Thus, the effectiveness of the conventional adsorbents is usually

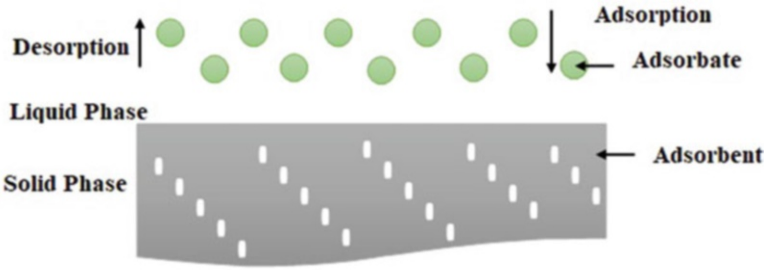


Fig. 1.1 Illustration of an adsorption terminology. Adsorption occurs when molecules in a liquid bind themselves to the surface of a solid substance. The adsorbate is accumulated on the adsorbent surface, and surface accumulation of adsorbate on an adsorbent is called adsorption

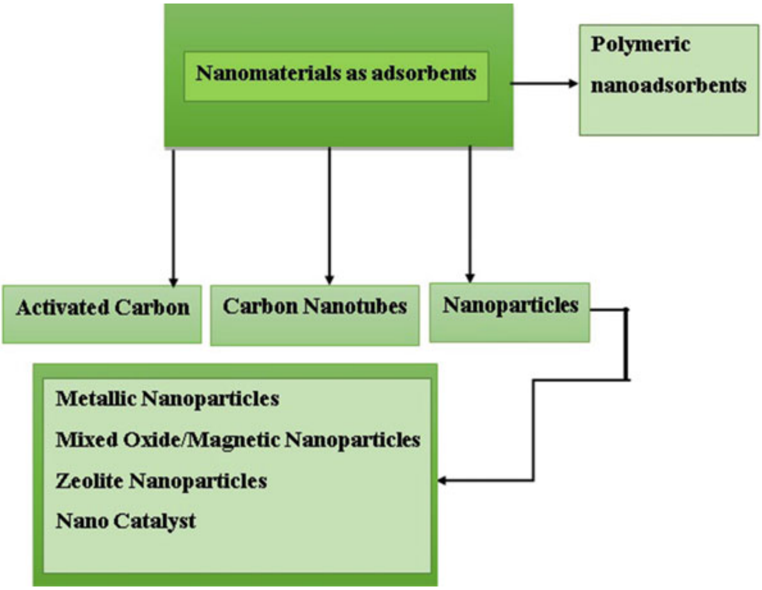


Fig. 1.2 Schematic illustration of the main nanomaterials used as adsorbents in wastewater treatment. This includes four classes: activated carbon, carbon nanotubes, nanoparticles and polymeric nanoadsorbents. These adsorbents have many exceptional morphological and structural properties that qualify them to be used as effective adsorbents to treat wastewater

limited by the surface area or active sites, the lack of selectivity and the adsorption kinetics (Qu et al. 2013). The adsorption kinetics of nanomaterials strongly depend on the adsorbate–adsorbent interaction. Furthermore, the adsorption kinetics of nanomaterials depend on the system conditions or parameters such as pH value, temperature and adsorbent dose. Hence, there is a need to assess the adsorption rate and understand the mechanism of adsorption for the design and synthesis of effective adsorbents and for the application of adsorbents to wastewater treatment.

Nanoadsorbents can be produced by using the atoms of those elements that are chemically active and have high adsorption capacity on the surface of the nanomaterial (Hu et al. 2010). The classification of nanomaterials as nanoadsorbents is illustrated in Fig. 1.2. These adsorbents have many excellent morphological and structural properties that make them suitable to be used as effective adsorbents in solving the problem of water paucity. Nanoadsorbents offer significant improvement over conventional adsorbents because nanoadsorbents have extremely high specific surface area, associated sorption sites, short intra-particle diffusion distance, tunable pore size and surface chemistry (Rakhi et al. 2016). Adsorption process relies solely on the adsorption coefficient K_d and the recitation partitioning of the pollutant, i.e. heavy metals or organic pollutants under equilibrium conditions (Khajeh et al. 2013). In the aqueous environment, the factors that affect the adsorption process are intermolecular forces, high surface area, adsorption activity, chemical activity, lack of internal diffusion resistance and high surface binding energy (Gupta et al. 2015).

The numerous types of nanoparticles for the adsorption of heavy metals include activated carbon and carbon nanotubes, manganese oxide, graphene, zinc oxide, magnesium oxide, titanium oxide, ferric oxides (Kyzas and Matis 2015) and polymeric nanoadsorbents. The importance of the application of nanoparticles and nanostructured materials as efficient and viable alternatives to activated carbon as adsorbents has recently increased. Factors controlling the nanoadsorbent properties are size, surface chemistry, agglomeration state, shape, fractal dimension, chemical composition, crystal structure and solubility (Anjum et al. 2016). Nanoadsorbents are considered composites since they involve materials made from two or more constituent materials with significantly different chemical or physical properties. When these properties are combined, a material with characteristics different from the individual components is produced.

Activated Carbon

Activated carbon is generally used to adsorb natural organic compounds (such as unwanted taste and odour), micro-pollutant compounds and chlorine, fluorine and synthetic organic chemicals from drinking water or wastewater. Adsorption efficiency is subject to the nature of activated carbon used, operating parameters and the composition of water. Activated carbons can be prepared from a variety of lignocellulose carbon-containing materials, such as rice hulls (Masoud et al. 2016; Ahmaruzzaman and Gupta 2011), pinewood (Pholosi et al. 2013), palm shell (Bt Fuadi et al. 2012; Kadir and Puade 2013), coke (Zamora et al. 2000), olive stone (Alslaibi et al. 2014; Spahisa et al. 2008; Malik 2004), sawdust (Susheela and Radha 2015), coconut shell (Ayub and Khorasgani 2014; Alslaibi et al. 2015). However, activated carbon used in treating wastewater is generally prepared from sawdust, coconut shell, peat, wood char, lignin, bone char (Khalkhali and Omidvari 2005). Activated carbon adsorption has numerous applications in removing pollutants from stream water, both in the field and in industrial processes, such as spill clean-up, groundwater remediation and drinking water filtration (Susheela and Radha 2015). Activated carbon has become the standard adsorbent for the reclamation of municipal and industrial wastewaters to potable water quality (Bhatnagar and Minicha 2006). Nonetheless, activated carbon is not effective for microbial contaminants, metals, nitrates and inorganic contaminants. Thus, there is a need to understand the several factors that impact the capacity of the adsorption of activated carbon. These factors govern the activated carbon's precise physical and chemical characteristics in order to increase activated carbon affinities regarding the elimination of microbial contaminants, metals and inorganic or organic species in water. These factors include the specific surface area and pore-size distribution, the volume of pores, the hydrophobicity of the compound, activated carbon surface chemistry, and the nature and concentration of the dissolved organics.

Activated carbon is often used as pre-treatment to protect other water treatment units, such as reverse osmosis, from possible damage (Chantharawong et al. 2017). The combination of ozonation with activated carbon is a very efficient technique, used for the removal of organic matters, including micro-pollutants (Lee et al. 2009). Activated carbon adsorption can yield between 10% and 30% removal of the total organic carbon from the saline source water. When activated carbon is combined with granular media filtration, the removal of organics in the pre-treatment system may be improved to over 40%. The addition of a layer of 0.3–0.5 m (1.0–1.5 ft.) of granular activated carbon on the top of the anthracite in gravity media is typically an effective measure for reducing dissolved organics. The measure for reducing dissolved organics occur during moderate and high-intensity algal blooms, to levels that can prevent the occurrence of excessive biofouling of the downstream reverse osmosis membranes (Voutchkov 2017). Activated carbon has difficulties associated with heavy metals and dye removal at ppb levels. However, carbon nanotubes have been used as nanosorbents to overcome the difficulty associated with heavy metals and dye removal at ppb levels (Sadegh et al. 2017). The removal of benzene and toluene from aqueous solution by multi-walled, single-walled and hybrid carbon nanotubes was evaluated (Bina et al. 2012). The authors concluded that single-walled carbon nanotubes showed a higher adsorption capacity for benzene and toluene removal than that for multi-walled carbon nanotubes and hybrid carbon nanotubes. Furthermore, between multi-walled carbon nanotubes and hybrid carbon nanotube, hybrid carbon nanotube shows better performance for benzene and toluene removal. Hence, the physicochemical characteristics of carbon nanotubes and the adsorbate should be investigated in order to tailor each carbon nanotubes for specific application.

Carbon-Based Nano Adsorbents

A carbon atom can form different types of allotropes. Diamond and graphite are the allotropes of carbon in three-dimensional structures. Carbon can also form low dimensions such as two-dimensional, one-dimensional or zero-dimensional allotropes, which are collectively known as carbon nanomaterials. Examples of such nanomaterials are one-dimensional carbon nanotubes and 0-dimensional fullerenes (Kaushik and Majumder 2015). The allotrope carbon nanotubes are unique nanostructure with extraordinary electronic and mechanical properties that directly depend on carbon nanotubes chirality and diameter (Saito et al. 1992). The exceptional properties become extremely attractive for adsorption, with high sensitivity, selectivity and efficiency (Gupta and Saleh 2013). Carbon nanotubes have shown excellent effectiveness than activated carbon on the adsorption of various organic chemicals. The high adsorption capacity of carbon nanotubes mainly stems from the large specific surface area and the diverse contaminate–carbon nanotube interactions. The available surface area for adsorption on individual carbon nanotubes is the external surface of carbon nanotubes (Rakhi et al. 2016). There are different types of carbon nanotubes, and they are usually categorised as single-walled nanotubes and multi-walled nanotubes, depending on carbon nanotube preparation procedures.

Carbon nanotubes contain a high specific surface area with highly assessable adsorption sites. Carbon nanotubes have a very large adsorption capacity and tough affinity to a wide variety of organic pollutants, and the process is affected by the physicochemical characteristics of both the adsorbent (carbon nanotubes) and the adsorbate (environmental pollutants) (Ma and Agarwal 2016). The different parameters that affect the adsorption capacity of carbon nanotubes are molecular size (Wang et al. 2009), aromaticity (Yang et al. 2006), configuration (Pan et al. 2008) and hydrophobicity (Gotovac et al. 2007). The hydrophobic surface of carbon nanotubes allows them to form loose bundles or aggregates in aqueous medium, which reduces the active surface area. These aggregates have high-energy sites for the adsorption of organic contaminants in water (Pan et al. 2008). The adsorption of bulky organic contaminants by carbon nanotubes occurs as a result of the availability of large pores in bundles and the availability of high accessible sorption sites in the carbon nanotubes (Ji et al. 2009). The availability of different adsorption sites on carbon nanotubes is determined by the molecular size of organic compounds. The molecular structure such as aliphatic and aromatic, the molecular volume and the presence of different functional groups strongly affect the interactions of the adsorbates with carbon nanotubes (Yang et al. 2008; Wang et al. 2010). An example was the investigation done on the adsorption mechanism for the removal of lead from water by using carboxylic functional group (COOH), functionalised on the surface of carbon nanotubes. High removal efficiencies were observed and were attributed to the strong affinity of lead, to the physical and chemical properties of the carbon nanotubes (Atieh et al. 2010).

Organic removal by carbon nanotubes is better than activated carbon for the removal of various organic waste chemicals. In the aqueous phase, carbon nanotubes form loose bundles or aggregates due to the hydrophobicity of the carbon nanotubes' graphitic surfaces, thereby reducing the effective surface area (Pan et al. 2008). These aggregates contain interstitial spaces and grooves that have high absorption energy for organic molecules (Yang and Xing 2010). Activated carbon possesses comparable measured specific surface area as carbon nanotube bundles. Activated carbon, however, comprises a significant number of microspores that are inaccessible to bulky organic molecules, such as many antibiotics and pharmaceuticals (Yang et al. 2008). Thus, carbon nanotubes have a considerably higher adsorption capacity than activated carbon for some bulky organic molecules because of carbon nanotubes' larger pores in bundles and the more accessible sorption sites (Zare et al. 2015). The major shortcoming of activated carbon is its low adsorption affinity for low molecular weight polar organic compounds. Carbon nanotubes strongly adsorb many of these polar organic compounds due to the diverse contaminant and carbon nanotube interactions, including hydrophobic effect, π–π interactions, covalent bonding, hydrogen bonding and electrostatic interactions (Chen et al. 2007; Yang and Xing 2010). The π electron-rich carbon nanotube surface permits π–π interactions with organic molecules with C=C bonds or benzene rings, such as polyaromatic hydrocarbons and polar aromatic compounds (Zare et al. 2015; Chen et al. 2007).

Solution chemistry, such as pH, ionic strength and the presence of natural organic compounds, also affect the interactions of carbon nanotubes (Zhang et al. 2009a). The change in pH in a solution has the capacity to activate the protonation–

deprotonation transition of the functional groups on a carbon nanotube surface and the ionisable contaminants. The change in pH will in turn cause a series of consequences, such as the formation of water clusters on the carbon nanotube surface (Zhang et al. 2011a, b). Furthermore, the ionic strength of the solution will affect the adsorption process through charge neutralisation (Zhang et al. 2011a, b) and cation bridging effects (Li et al. 2002). Lots of emerging contaminants are weak acids or bases. The chemical speciation of weak acids or bases, such as weak acid vs. ionised conjugate base or weak base vs. ionised conjugated acid, depends on weak acids or bases, acid dissociation constant (K_a) and solution pH (Ma and Agarwal 2016). With the novel confirmations proposed, new intermolecular forces can be involved in the adsorption of ionised compounds onto carbon nanotubes as a result of charge assisted molecular forces (e.g. charge assisted hydrogen bonding) (Teixido et al. 2011).

Functionalisation can be induced to the carbon nanotube surface through oxidation. Oxidised carbon nanotubes have high adsorption capacity for metal ions with fast kinetics. The first type of functionalisation usually involves oxidation by using acids or oxidants, triggering carboxyl groups to functionalise the defects and the ends of the carbon nanotubes (Lu and Chiu 2006). The adsorption capacity onto the surface of carbon nanotubes increased with the pH of the system, from acidic to alkaline. Thus, pH is one of the most important factors that affect the sites of dissociation of carbon nanotubes, hydrolysis, complexation and the precipitation of metal ions. The surface functional groups of carbon nanotubes (carboxylic acid, hydroxyl and carbonyls) absorb metal ions through electrostatic interactions and chemical bonding (Peng and Liu 2006; Liu et al. 2012a, b). Surface electrostatic interactions in solution also influence the sorption properties of materials in order to entrain environmental contaminants on the carbon nanotube sidewalls (Tavallai et al. 2012). Surface oxidation can therefore enhance significantly the absorption capacity of carbon nanotubes. Numerous investigations have shown that carbon nanotubes are better adsorbents for heavy metals (e.g. Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}) than does activated carbon (Lu and Chiu 2006; Lu et al. 2006; Li et al. 2003). The adsorption kinetics is fast on carbon nanotubes due to the highly accessible adsorption sites and the short intra-particle diffusion distance (Qu et al. 2013). Carbon nanotubes may not be a good alternative for activated carbon as wide-spectrum adsorbents. However, since the surface chemistry of carbon nanotubes can be tuned to target specific contaminants, they may have unique applications in polishing the steps to remove recalcitrant compounds or in the pre-concentration of trace organic contaminants for analytical purposes. These applications require a small quantity of materials and are hence less sensitive to material cost (Qu et al. 2013).

Nanoparticles

Nanoparticles can be produced from large structures of top-down approach by the use of ultrafine grinders, lasers and vaporisation, followed by cooling. For complex particles, nanotechnologists usually prefer to fabricate nanostructures by the bottom-up approach. The bottom-up approach is done by arranging molecules to form complex structures with new and useful properties (Samanta et al. 2016). Nanoparticles used as adsorbents for the removal of heavy metals must satisfy the following standards: (1) they must not be toxic, (2) they should have high adsorption capacity, (3) they should have the ability to adsorb pollutants in less concentration (ppb), (4) the adsorbed pollutants should be easily removed from the adsorbent surface and (5) they should be recyclable numerous times (Cloete 2010). Furthermore, the process should be reversible in order to get back the adsorbent. When nanoparticles, e.g. nanosized zero-valent irons are used as adsorbents, they aid in the separation of pollutants from water. Nanosized zero-valent irons also help to catalyse the chemical or photochemical oxidation process for the effective destruction of persistent contaminants (Nowack 2008). Research has shown that nanoparticles represent a new generation of environmental remediation technologies that can provide cost-effective solutions to some of the most challenging environmental clean-up problems. The following sub-sections will discuss the different types of nanoparticles used in wastewater treatment.

Metallic Nanoparticles

The term metallic nanoparticle is used to describe nanosized metals with dimensions (length, width or thickness) within the size range 1–100 nm. Metal nanoparticles have attracted a great attention over the last two decades as a result of the unique characteristics that metal nanoparticles possess when compared to other bulk metal equivalents. Metal nanoparticles' characteristics include large surface-area-to-volume ratio, large surface energies and tunable shapes. In order to control the properties of nanoparticles with respect to a particular shape, size and dispersity are imperative since they will determine the activity in the desired application (Campelo et al. 2009). Metal nanoparticle-based water treatment technologies are recently being pursued, and products have come out in the market (Daniel et al. 2014). The following sub-sections will review the application of metallic nanoparticles for wastewater treatment.

Silver Nanoparticle

Silver nanoparticles account for more than 23% of all nanoproducts. The wide application of the silver nanoparticles results in their inevitable release into the environment. Silver nanoparticles are recognised as excellent antimicrobial agents, and they can thus be used as substitute disinfectant agents. On the other hand, the release of silver nanoparticles can pose a threat to naturally occurring microorganisms (Zhang 2013). Silver nanoparticles can be prepared by various methods, including chemical reduction, electrochemical techniques and photochemical reduction (Sharma et al. 2009). Among these synthetic methods, chemical reduction is the most commonly used. However, toxic compounds, such as borohydrides, are usually involved. Studies have focused on green synthesis approaches in order to avoid the use of hazardous materials (Zhang 2013).

Wastewater contains a number of microorganisms that leads to the fast spread of diseases in humans and animals. Silver nanoparticles are known to possess antimicrobial properties against more than 700 microorganisms and are one of the wider spectra of antimicrobial agents. Silver nanoparticles target the microorganisms in more than three mechanisms; hence the microbes are unable to create mutations to exhibit resistance (Sironmani and Daniel 2011). The release of silver nanoparticles into domestic and industrial waste streams is unavoidable (Benn and Westerhoff 2008; Dobias and Bernier-Latmani 2008; Reidy et al. 2013), considering the high rate of use. The silver nanoparticles released can potentially cause adverse effects on the microbial communities in biological wastewater treatment systems due to the silver nanoparticles' antimicrobial properties. Hence, the release of silver nanoparticles or other forms of silver into the environment is a potentially serious issue. Considerable attention has been paid to the adverse effect of silver nanoparticles since the boom in the application of silver nanoparticles in consumer products (Sheng et al. 2015). Several investigations have been carried out concerning the release of silver from different sources, including paints (Kaegi et al. 2010) and textiles (Benn and Westerhoff 2008; Geranio et al. 2009). Some models have also been developed in order to predict the fate of silver in the environment (Gottschalk et al. 2009; Walser et al. 2011). A key measurement challenge in these investigations is to distinguish between nanoparticulate silver and silver ions. However, analytical methods, such as inductively coupled plasma mass spectrometry in the standard mode of operation and elemental analysis can confirm the presence of silver but cannot distinguish its form if the measurement is not preceded by a separation technique, such as ultracentrifugation. Again, methods such as transmission electron microscopy and other particle-sizing approaches have the difficulty of finding low concentrations of particles. In distinguishing between specific nanoparticles and background particles, combinations of transmission electron microscopy and energy-dispersive X-ray offer one approach but are time-consuming and costly (Reidy et al. 2013).

Silver nanoparticles are being evaluated to form antifouling membranes to be used in ultrafiltration processes (Mauter et al. 2011). The silver nanoparticles' intrinsic ability to kill microorganisms has recently been used against multidrug-resistant microbes and biofilm-forming bacterial cells (Sanyasi et al. 2016). Biofilm-forming microbes are not like normal microorganisms since they form a hardened cyst, which is difficult to act upon. Silver-nanoparticle-based polymeric membranes prevent such biofilm formation. Such antifouling membranes are essential in wastewater treatment (Daniel et al. 2014). Silver nanoparticles were recently loaded as silica adsorbents for the removal of pollutants and pathogens in wastewater. The pathogens were inactivated by silver nanoparticles loaded with silica by wet impregnation. The adsorbent prepared has potential against *Escherichia coli* and was described through Chick, Chick-Watson and Homs inactivation kinetic models. Concentration of 500 ppm of the adsorbent prepared showed complete inhibition with the shouldering or lag curve of inactivation and with k' values of 0.019 min^{-1}. After treatment, tannery, dairy and canteen effluents showed significant chemical oxygen demand reduction with a maximum adsorption capacity of 145, 142 and

69 mg/g, respectively. Regeneration of the spent adsorbent via alkali washing is a possibility and can be reused up to three cycles (Thamilselvi and Radha 2017). Silver nanoparticles have therefore, shown great potential for water purification and effectiveness for bacterial filtration.

Zero-Valent Iron Nanoparticles

Zero-valent iron is an elemental metallic iron that acts as a bulk reducing agent, converting oxidised materials, which may be toxic and soluble in water, into immobile solid forms, thereby releasing soluble Fe^{2+} in their place, and it further oxidises to Fe^{3+}. Such characteristics permit the use of zero-valent iron for an effective and reliable reduction of waterborne contaminants. Zero-valent iron nanoparticles are the most commonly used nanoparticles for the removal of heavy metal, owing to the high reactivity of zero-valent iron nanoparticles. Since they can be synthesised easily and are inexpensive, zero-valent iron nanoparticles are the most preferable (Daniel et al. 2014). The nanoscale zero-valent iron was reported as an ideal candidate for in situ remediation because of the nanoscale zero-valent iron large active surface area and high heavy metal adsorption capacity (Zhu et al. 2009). Nano-sized zero-valent iron is considered as an effective adsorbent and ideal technology for the in situ remediation of heavy-metal-contaminated groundwater (Yaacob et al. 2012). Nano-sized zero-valent iron has been reported to be an ideal candidate for the in situ remediation of arsenic-contaminated groundwater (Kanel et al. 2005; Kanel et al. 2006). Nano-sized zero-valent iron can also be a promising material for arsenic removal from drinking water as a result of the large active surface area and high arsenic adsorption capacity of nano-sized zero-valent iron (Zhu et al. 2009). However, adsorption has been reported as the most widely used technique for arsenic removal due to the numerous advantages of the process, which includes relatively high arsenic removal efficiencies (Singh and Pant 2004; Mohan and Pittman 2007), cost-effectiveness (Anjum et al. 2011), easy operation and handling (Jang et al. 2008) and no sludge production (Singh et al. 2015). Nonetheless, adsorption of arsenic intensely depends on the system's concentration and pH. At low pH, arsenate adsorption is favoured, whereas for arsenite, maximum adsorption can be obtained between pH 4 and 9 (Lenoble et al. 2002; Nicomel et al. 2016).

The nano-zero-valent iron is capable of exchanging toxic substances to nontoxic materials. The nano-zero-valent iron can be used to promote the reduction and precipitation of toxic and carcinogenic metals such as chromium(VI) to the more stable form of chromium, Cr(III) (Blowes et al. 2000). The entrapment of nanoscale zero-valent iron in chitosan beads for hexavalent chromium removal from wastewater was investigated by Liu et al. (2010). The nano-sized zero-valent iron was successfully entrapped in chitosan beads for the reduction of Cr(VI) from wastewater. The mechanism of the removal may include both physical adsorption of Cr (VI) on the surface or inside of chitosan-nano-sized zero-valent iron beads, followed by the reduction of Cr(VI) to Cr(III). The free amino groups and hydroxyl groups on chitosan may contribute little to hinder the formation of Fe(III)-Cr(III) precipitate.

Entrapment of nano-sized zero-valent iron in chitosan beads prevents the particles from aggregation and oxidation. The results indicate that there is no significant difference between the reaction rates of bare nano-sized zero-valent iron and entrapped nano-sized zero-valent iron. Cr(VI) reduction kinetics follows a pseudo-first-order rate expression. The study of the authors demonstrated that the entrapment of nano-sized zero-valent iron in chitosan beads has the potential to become a promising technique for in situ groundwater remediation. Adsorption of Cr (VI) followed the pseudo-first-order kinetics. Another study investigated the reductive immobilisation of chromium in wastewater by nanoscale zero-valent metal prepared from steel pickling waste liquor. The effects of pH, buffer substances, natural organic matter and hardness were evaluated in order to probe the impact of environmental factors. Removal of Cr(VI) benefited from a decrease in pH value and the presences of buffer substances and Ca^{2+}. Natural organic matter was found to be suppressive on the activity of zero-valent iron, coupled with the effect of Ca^{2+}, and the additive effect of natural organic matter was due to the non-interference of natural organic matter when operating under acidic condition. The nano-sized zero-valent iron was proven to be more effective (up to 40.6-fold) than zero-valent iron and nanoscale zero-valent iron for Cr(VI) removal. The removal efficiency of nano-sized zero-valent iron in wastewater was 182 ± 2 mg g^{-1}. The results indicated that nano-sized zero-valent iron was promising for the in situ remediation of Cr (VI) (Feng et al. 2011). Hence, nanosized zero-valent iron is considered an effective adsorbent and ideal technology for the remediation of metal ions in polluted water.

Mixed Oxide-Metallic Nanoparticles

Nanoparticles can be synthesised from oxides of various metals, such as titanium, iron, copper, zinc, manganese, magnesium, silica and aluminium. The combination of two metal oxides can be either a simple mechanical mixing involving weak van der Waals forces or a chemical possessing chemical linkages of the two types of metal oxide. The physicochemical properties of using a chemical possessing chemical linkage combination will be entirely different from the simple combination of individual oxides (Verma et al. 2013). Metal elements have a distinctive property to form oxides with a large variety of structural and electronic properties (Kaushal and Singh 2017). Mixed oxide nanoparticles exhibit high dielectric, ferro and pyroelectric properties. The synthesis of nanometre-scale mixed oxide particles, such as spinel ferrite (Khedr et al. 2006; Xu et al. 2009), Fe_3O_4 as pigment (Meng et al. 2005; Lie et al. 2017) and titanium-based mixed oxide (Klink et al. 2012), has been reported for their extraordinary magnetic, electrical and conducting properties. Metal oxide nanoparticles show higher extent of adsorption as compared to normal-sized oxide due to metal-ligand precipitation or the formation of ternary ligands (Stietiya and Wang 2014).

Mixed oxide nanoparticles containing titanium, silicon and aluminium of between 8 and 15 nm size range synthesised by using a combined sol-gel-hydrothermal method was recently used as a novel adsorbent for the removal of rhodamine 6G and methylene blue as cationic dyes from aqueous solution (Pal et al. 2016). The dye removal abilities of the nanoparticles from aqueous solutions were tested for different cationic dyes. All the mixed oxide nanoparticles revealed high and fast adsorption of cationic dyes, but the particles containing titanium and silicon turned out to be the best. The adsorption kinetics and equilibrium adsorption behaviour of the adsorbate-adsorbent systems can well be described by the pseudo-second-order kinetics and Langmuir isotherm model, respectively. Estimated thermodynamic parameters revealed that the adsorption process was spontaneous and was driven mainly by the electrostatic force between the cationic dye molecules and the negative charge on the nanoparticle surface. The highest dye adsorption capacity (162.96 mg MB/g) of the mixed oxide nanostructures containing titanium and silicon was associated to their high specific surface area and the presence of surface silicon-O^{δ}-groups. The following sub-sections will review the application of mixed oxide-metallic nanoparticles for wastewater treatment.

Titanium Oxide (TiO_2) Nanoparticle

Titanium oxide is preferred in anatase form, owing to its great photocatalytic activity. Titanium oxide is nontoxic and photochemically stable with high specific area. Titanium oxide has a more negative conduction band edge potential, such as higher potential energy of photo-generated electrons, and is relatively inexpensive. The performance of titanium oxide for certain technical applications is dominantly affected by its crystallite size, phase structure, surface area, impurity (dopant) type and concentration (Khajeh et al. 2013). The reactivity of titanium oxide nanoparticles in the removal of malachite green as model pollutant dye was reported by Abou-Gamra and Ahmed (2015). The adsorption isotherm of titanium oxide nanoparticles indicated an adsorption capacity of $6.3\ mg{\cdot}g^{-1}$. The value of enthalpy change ($\Delta H°$) for malachite green dye adsorption was 19 kJ/mol, which indicated the fact that the removal process was endothermic. The adsorption process followed a pseudo-second order rate equation, and the negative values of standard free energy ($\Delta G°$) suggested that the adsorption process is spontaneous.

Luo et al. (2010) confirmed the high absorption capacity, recovery and reuse of TiO_2 nanoparticles for the removal of As(III) from copper smelting industries' effluent wastewater. They found a reduction of 59 ± 79 μg LG1 of As(III) at pH 7 after 21 consecutive treatment cycles using regenerated TiO_2 containing 3890 ± 142 mg LG1 As(III) in the polluted water. Visa and Duta (2013) developed a substrate by hydrothermal processing from fly ash coated with TiO_2 and investigated its influence on the adsorption capacity of Cu^{2+}, Cd^{2+}, 1-hexadecyltrimetylammonium bromide and dodecylbenzenesulfonate from synthetic wastewater. They observed that the results indicate parallel adsorption of heavy metals and surfactants from mixed solutions. The investigation of these authors shows that the fly ash-TiO_2 substrate allows the efficient simultaneous removal of heavy metals and surfactant, resulting in treated waters that respect the discharge regulations. Visa, Duta and Andronic (2015) synthesised and tested the adsorption properties of a novel nanocomposite obtained using the hydrothermal method applied to a fly ash-TiO_2 slurry and hexadecyl trimethyl-ammonium bromide as surface controlling agent. They found that the nanocomposite substrate allowed reaching high removal efficiencies of multi-pollutant synthetic wastewaters, above 90%, both in adsorption and in photodegradation experiments, in optimised conditions. Hence, investigations have shown that titanium oxide is a type of nanoparticles that has been widely used as a powerful and efficient adsorbent for the removal of metal ions and surfactants from polluted water.

Iron Oxide (Fe_3O_4) Nanoadsorbents

In nature, iron oxides exist in many forms, such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3). The utilisation of iron-oxide-based nanomaterials with novel property and functionality has been widely studied due to the small size, high surface area and excellent magnetic property they possess (Oh and Park 2011). The use of iron-oxide-based nanomaterial is more attractive for the removal of heavy metal contamination from water due to some important features, such as small size, high surface area and the magnetic property that they possess (Teja and Koh 2009; Liu et al. 2012a, b; Warner et al. 2012). In addition, iron oxide nanomaterials with low toxicity, chemical inertness and biocompatibility show tremendous potential in combination with biotechnology (Huang et al. 2003; Gupta and Gupta 2005). Iron-oxide-based nanomaterials also offer minimal diffusion resistance with surfaces that can be modified with organic molecules, inorganic ions or some functional groups. The modification causes iron-oxide-based nanomaterial surfaces to have good potential for removing heavy metals. Nano-sized iron oxide particles exhibit super paramagnetism, an additional special property from common nanoparticles (Kaushal and Singh 2017). Magnetism is a distinctive physical property that independently helps in water purification by influencing the physical properties of contaminants in water (Xu et al. 2012). The combination of adsorption process and magnetic separation has been used extensively in water treatment and environmental clean-up (Mahdavian and Mirrahimi 2010). The magnetic property of iron oxide nanoparticles enables the easy separation of adsorbents from the system due to their low cost, strong adsorption capacity and enhanced stability. They can be reused for further application since the reusability of iron-oxide-based nanomaterials leads to a decrease in economic burden (Dave and Chopda 2014).

Some researchers have investigated the use of iron oxide nanomaterials at the laboratory and field tests for removing contaminants from wastewater (White et al. 2009; Girginova et al. 2010). Iron oxide nanomaterials are presently being used for organic contaminant adsorption, principally for the efficient treatment of large-volume water samples and fast separation by using a strong external magnetic field (Mahdavian and Mirrahimi 2010). A lot of laboratory experiments have been conducted in order to examine the removal efficiency of organic pollutants by using iron oxide nanomaterials for organic pollutants (Luo et al. 2011; Hu et al. 2010; Pan et al. 2012; Kumar et al. 2016). It has thus been recommended that Fe_3O_4 nanosorbents were effective and were economical adsorbents for the rapid removal and recovery of metal ions from wastewater effluents (Xu et al. 2012). Nevertheless, aggregation caused by high surface area-to-volume ratios of nanomaterials can control a number of important environmental processes, including ion uptake (Baalousha 2009). Furthermore, the numerous interactions that occurred in wastewater also affect the adsorption of metals. The type of contaminants and the two mentioned factors have now become a hot research field because they can restrict the efficiency of nanosorbents and the exploration of highly effective methods of modification of nanomaterials for enhancing the efficiency of nanosorbents. For example, carbon-coated Fe_3O_4 nanoparticles (Fe_3O_4/C) was applied as solid-phase extraction sorbents for the extraction of trace polycyclic aromatic hydrocarbons from environmental water samples (Zhang et al. 2010a). Fe_3O_4/C sorbents possess high adsorption capacity and high extraction efficiency due to the strong adsorption ability of carbon materials and the large surface areas of nanoparticles. Adsorption attains equilibrium rapidly, and analytes are eluted with acetonitrile readily. Salinity and solution pH have no obvious effect on the recoveries of polycyclic aromatic hydrocarbons, which avoids fussy adjustment to water sample before extraction. The advantages of surface modifications of nanoparticles are (1) the provision of oxidative stability by preventing them from oxidation and (2) the selective and specific uptake of heavy metal ions by providing specific reaction sites and functional groups. The functional groups, –COOH, $–NH_2$, –OH, –SH, etc., provide active sites for the exchange of metal ions. Chemical interactions, such as chemical binding and complex formation, and physical interactions such as electrostatic and Vander Waal’s interactions and the combination of modified ligand, are responsible for the adsorption of metal ions on the adsorbent surface (Wang et al. 2012). The review on the use of iron oxide nanoparticles as nanoadsorbents has shown the way to a new class of separation approaches for wastewater treatment. Hence, the future for nanoadsorbents based on iron oxide nanoadsorbent appears to be a very promising nanotechnology for the removal of organic pollutants from wastewater and pollutants from other polluted media.

Zeolite Nanoparticles

Zeolites are a class of materials with ordered micro-pores of less than 2 nm. Zeolites can be used for gas separation, catalysis and adsorption. Zeolites are low-density crystalline aluminosilicates that have regular one-, two- and three-dimensional micro-pores with well-defined pore sizes and shapes. When the well-defined structures of zeolites are combined with the hydrophilic/hydrophobic and porous nature of zeolites, the resultant materials become useful shape-selective molecular sieves and hosts for various guest molecules, such as organic and inorganic (Rahim et al. 2012). Efforts have recently been made in the preparation of zeolites with nanometre dimensions with enhanced accessibility of reactant molecules in order to achieve higher product yield and selectivity in catalytic reactions or fast diffusion in adsorption and ion-exchanged processes (Valtchev and Tosheva 2013; Mintova et al. 2013). Furthermore, zeolite nanoparticles with a size smaller than 200 nm can be stabilised in suspensions with different concentrations that are colloidal-stable and do not agglomerate with time (Mintova et al. 2013).

Zeolitic imidazolate frameworks are a subclass of metal organic frameworks with zeolite or zeolite-like topologies, which have numerous extraordinary features, such as chemical robustness and thermal stability (Park et al. 2006). There are various types of zeolitic imidazolate framework materials, but zeolitic imidazolate framework-8, a tetrahedral framework formed by zinc ions and imidazolate ligands with sodalite topology, is the most widely studied (Wu et al. 2007). Researchers have carried out extensive work on the synthesis zeolitic imidazolate framework-8 for adsorption in wastewater treatment (Lin and Chang 2015; Wu et al. 2014; Liua et al. 2015). Zeolitic imidazolate framework-8 has been used as an attractive sorbent for arsenic removal because of the ultrahigh porosity, high chemical stability and hydrophobic nature of zeolitic imidazolate framework-8. The feasibility of the adsorptive removal of arsenic by zeolitic imidazolate framework-8 nanoparticles was systematically investigated by Jiana et al. (2015). The synthesised zeolitic imidazolate framework-8 nanoparticles exhibited a high surface area of 1063.5 m^2/g and were of between 200–400 nm in particle size. The kinetics and isotherm data of arsenic adsorption on zeolitic imidazolate framework-8 were well fitted by pseudo-second-order and Langmuir models, respectively. The maximal adsorption capacities of As(III) and As(V) at $T = 25$ °C and pH 7.0 were of 49.49 and 60.03 mg/g, respectively. The zeolitic imidazolate framework-8 nanoparticles were stable at neutral and basic conditions. Zeolitic imidazolate frameworks have also been used for the removal of phthalic acid and diethyl phthalate from aqueous solutions, via adsorption (Khan et al. 2015). The adsorption capacity of the zeolitic imidazolate framework-8 for phthalic acid was considerably higher than that of a commercial activated carbon or other typical metal–organic frameworks. Due to the surface area, the pore volume of the adsorbents showed no favourable effect on the adsorption of phthalic acid. Thus, the remarkable adsorption with zeolitic imidazolate framework-8 suggests a specific favourable interaction (electrostatic interaction) between the positively charged surface of zeolitic imidazolate framework-8 and the negatively charged phthalic acid anions. In addition, acid-base interactions also have a favourable contribution in the adsorption of phthalic acid. The contribution is based on the adsorptive performances of pristine and amino-functionalised metal-organic frameworks and the adsorption over zeolitic imidazolate framework-8 at acidic condition ($pH = 3.5$). These assessments showed that zeolite nanoparticles are promising adsorbents that recently found broad application in wastewater treatment.

Nanocatalysts

Nanocatalysts are also effective in removing contaminants from wastewater due to their unique physical and chemical characteristics. Owing to nanocatalysts' high surface-to-volume ratio and shape-dependent properties, nanocatalytic substances, such as zero-valent metal, semiconductor materials and bimetallic nanoparticles, are extensively used in water treatment. The properties of nanocatalysts are a result of the increase in nanocatalyst catalytic activity at the surface (Samanta et al. 2016). The catalytic activity enhances the reactivity and degradation of environmental contaminants, such as organochlorine-based pesticides, halogenated herbicides, azo dyes, polychlorinated biphenyls and nitro aromatics (Zhao et al. 2011). Nanocatalysts, specifically those made from inorganic materials, such as semiconductors and metal oxides, are gaining considerable attention in the treatment of wastewater. The most common kinds of nanocatalysts that have been used for wastewater treatment are (1) photocatalysts (Dutta et al. 2014), (2) Fenton-based catalysts (Kurian and Nair 2015) for improving the chemical oxidation of organic pollutants (Ma et al. 2015) and antimicrobial actions (Chaturvedi et al. 2012) and (3) electrocatalysts (Tung et al. 2013). Here, photocatalysts was discussed as one of the most promising technologies for wastewater treatment.

Heterogeneous photocatalysis has established its worth toward meeting the challenges posed by cost-effective wastewater treatments. Despite the massive number of pollutants that have been the subject of investigation of photocatalytic treatment, knowledge on the photo-initiated advanced oxidation processes for the conversion of hazardous emerging chemical substrates, introduced to the water ecosystem, is still incomplete (Martínez-Huitle and Andrade 2011). A nanotechnology approach can be used to harness the photocatalytic capabilities of titanium dioxide (TiO_2), the most extensive catalyst investigated in the past decades (Lu et al. 2016). TiO_2 produces an electron/hole (e^-/h^+) pair upon absorbing an ultraviolet photon, which later either migrate to the surface and form reactive oxygen species or undergo undesired recombination. The photo activity of nano-TiO_2 can be improved by optimising particle size and shape, reducing e^-/h^+ recombination by noble metal doping, maximising reactive facets and surface treatment in order to enhance contaminant adsorption (Qu et al. 2013). The size of TiO_2 contributes a significant part in its solid-phase transformation, sorption and (e^-/h^+) dynamics. Among the crystalline structures of TiO_2, rutile is the most stable for particles larger than 35 nm, while anatase, which is more efficient in generating reactive oxygen species, is the most stable for particles smaller than 11 nm (Fujishima et al. 2008). When particle size is reduced to a few nanometres, surface recombination dominates, thereby decreasing photocatalytic activity. Thus, the photocatalytic activity of TiO_2 has a maximum, owing to the interplay of the mechanisms producing an electron/hole (e^-/h^+) pair upon absorbing an ultraviolet photon, which lies in the nanometre range (Qu et al. 2013). However, heterogeneous photocatalysis, using the industrial mass product TiO_2, was recognised as an advanced oxidation process that offers an important advantage over other existing oxidative technologies: it does not require the use of hazardous oxidative substances, such as hydrogen peroxide or ozone. Furthermore, TiO_2, which is preferably not consumed due to TiO_2 usage as a catalyst, is non-toxic, chemically stable and highly photocatalytically active and inexpensive (McCullagh et al. 2011). The photocatalytic and adsorption abilities of the TiO_2-adsorbent nanocomposites prepared via a facile wet chemical method were investigated by using Methylene Blue as the model pollutant (Zhang et al. 2010b). Synergistic effects between adsorption and photocatalysis were observed with the assistance of visible light irradiation, and all TiO_2-adsorbent nanocomposites achieved higher Methylene Blue removal rates than the adsorption process alone.

The hybrid process of activated carbon adsorption-heterogeneous photocatalytic oxidation has also attracted a lot of attention. Studies have been done with simple mixtures of activated carbon (or other adsorbents) and photocatalysts (Matos et al. 2007; Gulyas et al. 2009; Baransi et al. 2012). Investigations have also been carried out with TiO_2 (or other semiconductor photocatalysts), coated on activated carbon (Tryba et al. 2003; Zhang et al. 2005; Ao et al. 2008; Gu et al. 2010; Delmas et al. 2014). The interaction observed in the photocatalytic oxidation-activated carbon combination process is usually measured in terms of the synergy factor, the ratio of the photocatalytic oxidation rate constant in the presence ($k_{\mathrm{PCO\_AC}}$) and the absence (k_{PCO}) of activated carbon, as shown in Eq. 1.1. (Xu, 2011; Gulyas et al. 2013):

$$\mathrm{SF} = \frac{k_{\mathrm{PCO\_AC}}}{k_{\mathrm{PCO}}} \tag{1.1}$$

The purpose for the synergy is the short diffusion pathways for organic molecules from the adsorbent to the photocatalyst particles, which directly stick to the activated carbon (Lim et al. 2011). The synergetic effect has been explained by the formation of a common contact interface between the different solid phases, in which activated carbon acts as an efficient adsorption trap for the organic compounds (Andriantsiferana et al. 2015). Hence, the pollutant is then more efficiently shifted to the TiO_2 surface (Wang et al. 2007). Furthermore, synergy factors for the photocatalytic oxidation-activated carbon hybrid process can be associated to the interfacial areas between activated carbon and photocatalyst particles as the synergy rises with an increase in the interface contact between TiO_2 and activated carbon (Gulyas et al. 2013). Nonetheless, when the contact area exceeds 50% of the total surface of the photocatalyst, the synergetic effect decreases (Matos et al. 2009). Due to the unmanageable diversity of visible light photocatalysts, comparative investigations with respect to stability and photocatalytic efficiency are urgently needed in order to identify the most promising candidates (Gulyas 2014). However, innovative photocatalysts and nanophotocatalyst-adsorbent composites should be researched and tested for their long-term stability. Improving contaminant adsorption through the modification of the photocatalyst surface is one route for enhancing photocatalytic activity due to the short life time of reactive oxygen species; thus, the aspect of photocatalytic activity of nano-TiO_2 should also be succinctly researched.

Polymeric Nanoadsorbents

Polymeric nanoadsorbents are synthetic adsorbents, with characteristics such as porosity, pore structure and the nature of its adsorbing surfaces. Polymer-based nanoadsorbents are one of the most important recent developments in sample pre-treatment processes. Organic polymers as a system into which inorganic nano-sized materials can be inserted for improving their chemical, mechanical and very good thermal stability over a wide range of pH and sorption properties are now in use. Furthermore, organic polymer as a bed or template for synthesising and growing nanoparticles is being considered among the adsorbents of interest (Khajeh et al. 2013). Nanopolymer spheres can also be listed as desirable adsorbents for separation purposes. Polymer-based nanoadsorbents have been extensively employed in the solid phase extraction to pre-concentrate various metal and organic contaminants. Organic compounds can be adsorbed by the interior hydrophobic shells, whereas heavy metals can be adsorbed by the tailored exterior branches (Khajeh et al. 2013). For example, Fe_3O_4 magnetic nanoparticles were modified with 3-aminopropyltriethoxysilane and copolymers of acrylic acid and crotonic acid as polymer shells were prepared for the removal of metal ions. The utilisation of a polymer shell restrained inter-particle aggregation and enhanced the dispersion stability of the nanostructures. The polymer-modified magnetic nanoparticles effectively removed metal ions such as Cd^{2+}, Zn^{2+}, Pb^{2+} and Cu^{2+} from the aqueous solution with high maximum adsorption capacity at pH 5.5. Such nanoadsorbent is reusable, in at least four cycles (Ge et al. 2012).

A highly efficient bioadsorbent for the removal of anionic compounds such as dye from textile wastewater by preparing a combined chitosan-dendrimer nanostructure was produced (Sadeghi-Kiakhani et al. 2013). The bioadsorbent is biodegradable, biocompatible and nontoxic. Removal rates of certain dyes, up to 99%, was achieved. A polymeric hybrid sorbent (ZrPS-001) was also fabricated for the improved sorption of metal ions such as lead, cadmium and zinc ions from the aqueous solution by impregnating $Zr(HPO_3S)_2$ (i.e., ZrPS) nanoparticles within a porous polymeric cation exchanger D-001. The negatively charged groups bound to polymeric matrix D-001 resulted in a pre-concentration and permeation enhancement of target metal ions prior to sequestration. These nanoparticles are expected to sequester heavy metals through an ion-exchange process (Zhang et al. 2008). The most obvious advantages for polymer-inorganic nanoscale hybrids are good adsorption capacity and good chemical stability in a wide pH range due to the ease of functionalisation through different polymeric units, such as epoxide and epoxy. Furthermore, regeneration and reuse of the polymer inorganic nanoscale hybrid adsorbents is more responsive than that of solo nanoparticle sorbents. Although polymeric nanoadsorbents are outstanding materials for the removal of metal ions from water/wastewater, with respect to their structures, pore sizes and tunable functional groups, however, the ability to make selective for a given pollutant is still a mission (Kunduru et al. 2017). The adsorbing capacities of these materials are rather low, and regeneration is required and at a high cost (Pan et al. 2008). Research still needs to be done to be able to make polymeric nanoadsorbents selective for a given pollutant, putting into consideration the regeneration, reuse and cost of polymeric nanoadsorbents.

1.4 Nanomembranes

Nanomembranes can be defined as filters with free-standing structure of thickness in the range of 1–100 nm, which separate liquids and gases at the molecular level. Such membranes are made from organic polymers, combined with a mesh of nanoparticles. The size of the pores in the mesh prevents or permits the passage of differently sized molecules. Being quasi-2D, they display a host of rare properties that are useful for various applications in energy harvesting, sensing, optics, plasmonic, wastewater treatment, biomedicine, etc. Other notable characteristics include the formation of nanoparticle fillers into the nanomembrane scaffold, nanomembrane surface sculpting and modification through patterning. Further notable characteristics include the formation of nano porous arrays and the introduction of ion channels, similar in function to those in biological nanomembranes (Jaksi and Matovic 2010). Such dimensions make them a hybrid between micro and nano systems since their thicknesses remain nanometric with their lateral dimensions. Molecularly designed at the nanometre-scale level, by using membranes such as polymers, offers a great potential for high selectivity and high fluxes (Kumar et al. 2014). Nanoscale control in the fabrication of membrane can yield membranes of great selectivity and low-cost wastewater treatment.

In order to understand the effects of the pore size and the pore shape of the nanomembrane or the modified pore surface, the likely osmotic flow and the electric field variability within nanopores is very important. The combination of these parameters controls the flux of macromolecules through nanopores (Stroeve and Ileri 2011). Nanomaterials can serve as the basis for new nanomembrane processes based on passive diffusion or active transport. New materials may also be used in conjunction with membranes in order to create new nanomaterial-membrane reactors (Wiesner et al. 2007). The recent progress in nanotechnology combined with the membrane separation process has been recognised as a feasible and effective approach for enhancing the performance of the membrane, with its synergistic effects for water and wastewater treatment (Pendergast and Hoek 2011). Thus, advances in nanomembrane technologies have given immeasurable facilities and opportunities to purify water, even at the ionic levels. Subsequent sub-sections review the description of the various innovations in nanomaterial-based membranes used for water purification in order to protect the environment.

1.4.1 Carbon Nanotube Composite Membranes

Due to the high specific surface area, high mechanical strength, excellent chemical inertness and outstanding water-transport property of carbon nanotubes, carbon nanotubes have received widespread interests in the construction of new composite membranes for water treatment applications (Das et al. 2014; Lee and Park 2016). As a result of the high bacterial adsorption capacity possessed by carbon nanotubes, research studies have revealed their applications as an efficient adsorbent or nanofilters for the removal of pathogens. In addition, intensive research efforts are currently focusing on the functionalisation of carbon nanotubes in order to develop a biosensor for the detection of pathogens (Lichtfouse et al. 2012). Considering the fact that carbon nanotubes possess antimicrobial properties, the biosensor will have the capacity to concentrate and detect pathogens, adding to the selective differentiation of bacterial strains ascribed to the recognition properties of biomaterials. Thus, carbon nanotubes are gaining considerable interest in the development of treatment-based and sensor-based applications in the water and wastewater treatment industries (Lichtfouse et al. 2012). The blends of carbon nanotubes mixed matrix membranes are used for the fabrication of improved disinfection or antifouling membranes. The main disadvantage for the production of carbon nanotubes blended mixed matrix membrane is the solubilisation problem that occurs during the preparation of the casting solution with carbon nanotubes. Carbon nanotubes are insoluble in water and organic solvents, and thus they affect the large-scale fabrication of mixed matrix membranes (Ajayan 1999). Carbon nanotubes have been recommended to be functionalised with polymer groups so that they become structurally similar to the bulk polymer matrix, and then carbon nanotubes get dispersed in polymer to ensure homogenous membrane properties (Lin et al. 2007). For example, Majeed et al. (2012) modified polyacrylonitrile membranes with hydroxyl functionalised carbon nanotubes via a phase inversion process, and they discovered that the mechanical stability and the transport properties of the modified membranes were clearly enhanced by the introduction of carbon nanotubes. Likewise, Yang et al. (2016) fabricated functional polymer brush grafted carbon nanotube-polyethersulfone membranes via a phase inversion process. The resulting composite membranes showed enhanced anti-fouling ability, antibacterial activity and toxin removal ability, which might satisfy diverse separation and purification needs. Yin et al. (2013) also demonstrated that the integration of oxidised carbon nanotubes into polysulfone membranes can synergistically advance permeability and anti-fouling ability.

The specially aligned carbon nanotubes are of special interest for the fabrication of carbon nanotube membranes. The pore diameter has distinct effects on the transportation of water through the membranes that consist of aligned carbon nanotubes (Das et al. 2014). Well-aligned carbon nanotubes can serve as robust pores in membranes for water desalination and decontamination applications (Elimelech and Phillip 2011). The hollow carbon nanotube structure offers frictionless passage of water molecules, and this makes them appropriate for the advancement of high fluxing separation techniques. Suitable pore diameters can constitute energy barriers at the channel entries, thereby rejecting salt ions and permitting water to pass through the nanotube hollows (Corry 2008). The diffusion of water molecules through hollow carbon nanotubes is a highly coordinated movement and can be well described by the ballistic motion of water chains (Striolo 2006). The density, pore architectures and thickness of carbon nanotubes, significantly affect the morphology of membrane, water permeability and the ability of the carbon nanotube membranes to desalinate. Membrane thickness and water permeability inversely relate with each other (Zhu et al. 2008). Hence, increasing membrane thickness decreases water flux and selectivity. Therefore, noble observation is very essential in order to grow aligned carbon nanotubes by a suitable membrane synthesis process. Carbon nanotube membranes have demonstrated possible potentials to resolve water problem since they play significant roles in water passage, permeability and anti-fouling ability.

1.4.2 Nanoparticle-Based Membranes

Numerous developments have been made in the investigations of nanoscale structures for the treatment of wastewater. The advancement of particles at the nanoscale level has contributed extensively to the production, modification and shaping of structures that were used in different applications, viz., industrial, health and environmental (Seitz et al. 2011; Bhattacharya et al. 2013). Nanoparticles can be incorporated in the field of membrane science in order to improve the performances of membrane; as a result of nanoparticles convenient operation and mild conditions. Several investigations have been conducted in order to increase the hydrophilic properties of the polysulfone membrane surface. These studies can be divided into three categories, i.e. the blending of polysulfone with hydrophilic nanoparticles such as SiO_2, ZrO_2 and TiO_2; grafting with hydrophilic polymers, monomers or functional groups; and coating with hydrophilic polymers (Yanan et al. 2007). Blending provides the benefit of preparing artificial membranes with outstanding separation performance, good thermal and chemical resistances and adaptability to withstand the harsh wastewater environments (Maximous et al. 2009). Metal nanocomposite membranes can remediate two types of fouling, viz., membrane fouling as a result of organic matter and biofouling (Richards et al. 2012). Past studies have examined the efficiency of Ag, TiO_2, Al_2O_3 and ZrO_2 nanoparticles as membrane fillers for wastewater treatment. Zodrow et al. (2009) established that the incorporation of silver nanoparticles into polysulfone ultrafiltration membranes exhibited antimicrobial properties toward a variety of bacteria, including *Escherichia coli* K12, *Pseudomonas mendocina* KR1 and the MS2 *bacteriophage*. Nanosilver incorporation also increased membrane hydrophilicity by reducing the potential for other types of membrane fouling.

Studies of nanotechnology have suggested that improved membrane performance can be attained when nanoparticles are used for photocatalytic water contaminant degradation, which are very stable under ultraviolet light and in the presence of reactive oxygen species. Applying ozone as pre-treatment generally indicates a reduction in membrane fouling (de Velasquez et al. 2013), especially in cases where ozonation caused a significant degradation of influent biopolymers and/or colloidal natural organic matters (Barry et al. 2014). The unrecycled TiO_2 nanoparticles in water can also lead to environmental problems (Song et al. 2012). A substitute to this process is to immobilise TiO_2 by blending it with polyvinylidene difluoride in the membrane casting solution in order to prepare organic-inorganic composite membranes (Cao et al. 2006). The method incorporates membrane separation and photocatalytic degradation into a single operation. The pre-treated membrane will have the capability to degrade natural organic matter and decrease membrane fouling during the ultrafiltration process under ultraviolet light. The TiO_2 hybrid membrane was investigated for its photocatalytic efficiency in the destruction of Escherichia coli (*E. coli*) as a model bacterium under ultraviolet light illumination. The photocatalytic bactericidal destruction was remarkably high for the TiO_2 hybrid membrane under ultraviolet illumination (Kwak and Kim 2001). TiO_2 can be physically blended into the casting solution with polyvinylidene difluoride and polyethylene glycol in order to fabricate TiO_2-doped polyvinylidene difluoride -polyethylene glycol membranes. The TiO_2-doped polyvinylidene difluoride-polyethylene glycol membranes exhibit small pore sizes, increased hydrophilicity and anti-fouling abilities in preliminary tests (Song et al. 2012). Although TiO_2 is excitable under visible and ultraviolet light, TiO_2-doped polyvinylidene difluoride-polyethylene glycol membranes have shown improved self-cleaning ability, anti-bactericidal properties and anti-fouling abilities under ultraviolet light exposure.

1.4.3 Ceramic Membranes

Ceramic membranes are presently receiving substantial interest as nanomembranes for wastewater treatments due to their numerous properties, such as high mechanical strength, thermal stability, high flux, lower life-cycle cost and resistance to corrosive environments. Ceramic membranes have the capability of experiencing higher feed water recoveries. Ceramic membranes operate with more efficient backwash operations by using high pressures, operate at extended backwash intervals and have low chemical cleaning requirements while experiencing long membrane life without breakage. Ceramic membranes are becoming cost-competitive with conventional polymeric membranes for water and wastewater applications and have a strong potential for drinking water treatment (Lehman et al. 2008). However, they usually need relatively high initial investment cost when compared to polymeric membranes when they are used in a water treatment process. Thus, the life cycle cost analysis should be performed in order to evaluate its economic feasibility if ceramic membranes are considered to be applied in a water treatment plant (Xing et al. 2013). Depending on their pore sizes, ceramic membranes can be classified as (1) microfiltration, (2) ultrafiltration, (3) nanofiltration, (4) reverse osmosis, (5) pervaporation, (6) gas separation or (7) ceramic membrane reactors. Oxides such as Al_2O_3, TiO_2, ZrO_2, SiO_2 and their combinations are some of the common ceramic membrane materials (Park et al. 2015). Thin ceramic membranes are difficult to fabricate and to handle due to their brittleness. Therefore, composite ceramic filtering cells are frequently used for microfiltration and ultrafiltration. The composite cell is typically made up of two or more layers with different pore diameters. The ceramic filtering cell with a membrane coating consists of a macroporous substrate with thickness of one to several millions or one or several thin microporous membrane layers (Komolikov and Blaginina 2002). Substrates are constructed by utilising metal oxide powders, to which binders and plasticisers are added, and the resulting mixture is compressed, extruded or slip cast (Cortalezzi et al. 2002). The metal oxide particles are deposited on the support layer and sintered to form a chemically attached membrane skin. The pore size of a membrane is, therefore, determined by the size of the deposited particles (Yu et al. 2003; Zhang et al. 2009a, b) and by the sintering conditions employed (Jones et al. 2001; Choi et al. 2007). The pore diameter of the membrane layer should match to the size of the particle subjected to separation. Hence, the fact that the separation layer on the ceramic membrane should be porous and thin is very important while still ensuring that the layer covers the membrane surface completely in order to attain high permeability. The preparation of ceramic membranes by using metal oxide nanoparticles gives additional functionalities that can catalyse reactions in order to degrade foulants under oxidisation conditions. With respect to functionalities, ceramic membrane materials provide considerable opportunities for the fabrication of nanoparticle-based membranes. Casting nanoparticles onto ceramic materials yields more nanoscale pore sizes than the conventional sintering of ceramics (DiGiano 2008). One vital factor to note is that an increase in the catalytic properties of ceramic membranes, fabricated with catalytic nanoparticles, is postulated under extreme chemical conditions. However, the concern about optimising functional membranes still has stirred interest in fabricating conditions and expanding their functionalities (Kim and Van der Bruggen 2010).

1.4.4 Nanofiber Membranes for Water Purification

Nanofibres are unique nanomaterials as a result of the nanoscaled dimensions in the cross-sectional direction and the macroscopic length of the fibre axis they possess. The characteristics of nanofibre are shown in Fig. 1.3 (Matsumoto and Tanioka 2011). As a result of very fine dimensions and high surface-area-to-volume ratio of nanofibres, they are ideal materials for a variety of high-value applications, including filtration, composites, protective textiles, optical and chemical sensing, photovoltaic cells, tissue engineering and drug delivery (Zander et al. 2016). Electrospinning is a novel technology commonly used for the fabrication of nanofibre articles with diameters less than 100 nm (Li and Xia 2004). The composition of the nanofibre material can be controlled in order to attain desired properties and functionality (Botes and Cloete 2010). Nanofibre formation thickness and its morphology development by electrospinning are influenced by various process parameters, such as distance between the syringe needle tip to the ground collection plate and electric potential at the capillary tip. Furthermore, spinning conditions such as solution temperature, humidity, surface tension and air velocity in the electrospinning chamber, solution properties and solution concentration also influence nanofibre formation (Wang and Hsieh 2004; Wang 2007). Owing to the characteristics of high surface area to volume, fine fibre diameters and small pore sizes, nanofibre membranes represent ideal candidates for next-generation microfiltration materials. The

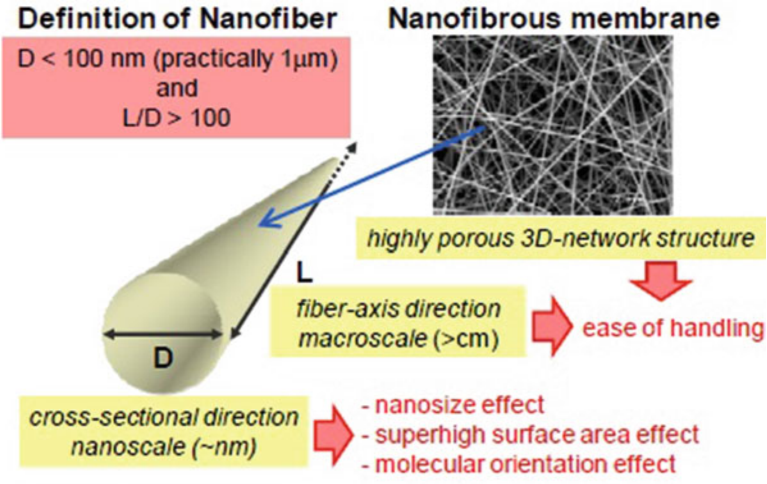


Fig. 1.3 Characteristics of nanofibre membranes with the nanoscaled dimensions in the cross-sectional direction and the macroscopic length of the fibre axis. The functionalities of the nanofibre membranes are dependent on their nanoscaled size, high specific surface area and high molecular orientation (Adapted from Matsumoto and Tanioka 2011)

functionalities of the nanofibre membranes are dependent on their nanoscaled size, high specific surface area and high molecular orientation (Matsumoto and Tanioka 2011). The functionalities can be controlled by fibre diameter, the internal structure of the nanofibres, surface chemistry and topology. Additional properties that make nanofibre membranes ideal candidates are high flexibility and surface modification capability (Balamurugan et al. 2011). Electrospun membranes can overcome some limitations such as low flux and high fouling due to the physical structure of the pores and size distribution owing to the highly interconnected and asymmetric nature of the pores (Wang et al. 2005). Recently, the use of nanofibres in wastewater treatment has been explored, and it has shown great potential as a replacement material for commercial membranes (Zander et al. 2016). JilíIek et al. (2017) fabricated self-sustained electrospun polyurethane nanofibre membranes, and the membranes were tested on a direct-contact membrane distillation unit in an effort to find the optimum membrane thickness to maximise flux rate and minimise heat losses across the membrane. Furthermore, salt retention and flux at high salinities up to 100 g/kg were evaluated. The highest flux was achieved with the thinnest membranes, and the best energy efficiency was achieved with the thickest membranes. All membranes had salt retention above 99%.

Though nanofibre is a promising material used in treating wastewater, the mechanical strength of the nanofibres limits their application in real life. For example, studies have proven the superior mechanical performance of electrospun nanofibres; however, problems persist with low tensile strength and young moduli, hence mechanical instability (Huang et al. 2004; Hansen et al. 2005; Greiner and Wendorff 2008). The problems can be mainly ascribed to the low degree of orientation and chain extension of the polymer chains along the fibre axis (Yao et al. 2014). However, some efforts have been made recently to overcome these mechanical restrictions. Novel high-performance polyamide, polyacrylonitrile and polyvinylidene fluoride nanofibres were recently fabricated using industrial production Nanospider equipment for liquid filtration as microfilters. A feasible approach in preparing mechanically strong nanofibre web work was developed. The mechanical strength of the nanofibres was improved using the special lamination technique on a supporting layer (Yalcinkaya 2017). The author found that the mechanical strength of the nanofibres enhanced more than five times, while high porosity and liquid permeability were retained. The separation results indicated that nanofibres have a potential to be used in liquid filters once the mechanical limitations have been overcome.

The increase in mechanical properties of polyvinyl alcohol nanofibre mats via physical crosslinking with solvent vapor treatment using organic solvents; dimethyl sulfoxide; N, N-dimethyl formamide; and methanol was recently studied. The authors observed that the tensile strength increased by over 60%, 90% and 115% after solvent vapor treatment with N, N-dimethyl formamide at a temperature of 40 °C for 2 h, 4 h and 8 h, respectively, compared with untreated polyvinyl alcohol nanofibres. In addition, Young's modulus of polyvinyl alcohol nanofibre mats also increased after N, N-dimethyl formamide treatment (Rianjanu et al. 2018). As a comparison, dimethyl sulfoxide and methanol were also used in solvent vapor treatment because of the differences in their polymer solvent affinity. Results showed that the highest improvement (100%) in mechanical strength was obtained using N, N-dimethyl formamide. Their study showed that solvent vapor treatment offers a simple and inexpensive method that provides excellent results and is a promising alternative treatment for use in increasing the mechanical properties of electrospun nanofibres (Rianjanu et al. 2018). Though the shortcoming of the mechanical restriction can be overcome, however, a three-dimensional nanofibre membrane network assembly offers good mechanical properties and good handling characteristics (see Fig. 1.3). Nonetheless, properties of the nanofibres, such as electrical and optical properties, including mechanical properties, depend on the intrinsic properties of a polymer and the internal structure of the fibres.

1.5 Patent and the Industries Providing Nanotechnology Products

Inventions in the advancement of novel nanotechnologies for the treatment of wastewater are among the most thrilling and seem to be promising technologies. The influence of nanotechnology on the economy can be measured through intellectual property activities as a result of the dynamic importance of securing innovations and technological interests (Hashem 2014). However, several types of intellectual property protection can administer innovations associated to nanotechnologies; the most important intellectual property right will be patents (Seear et al. 2009). Normally, the initial stage to bring any given novel technology to society is through the patent system (Olvera et al. 2017). Furthermore, industrial facilities have provided incentives to develop novel nanotechnologies and improve the performance of existing technologies (Tansel 2008). Some patented work and industrial efforts are discussed here in order to have a deeper insight into the inherent societal benefits of the use of nanotechnologies in wastewater treatment. There are, however, no precise methods to determine the social impact of a nanotechnological breakthrough (Olvera et al. 2017).

1.5.1 Patents on Nanoparticles for Its Applications in Wastewater Treatment

Saien (2010) patented the use of TiO_2 for the treatment of refinery wastewater. The patent was related to a photocatalytic reactor system and photo-degrading method used for eliminating organic and high molecular oil contaminant (or pollutants) from industrial wastewater. The invention was highly efficient, is compatible with the environment and does not require secondary or additional treatments. The invention has an industrial interest as the method used is considered an alternative or synergetic process for biological degradation, having high residence times, which is required to provide significant carbon oxygen demand removal. Girgis and Aziz (2013) patented the use of nano alloys ($ZnFe_2O_4$ alloy, Co-Ni-B alloy, $MnFe_2O_4$, $ZnMn_2O$ alloy) in wastewater treatment by introducing a new nanotechnology technique based on nanoparticles for wastewater treatment with an efficiency of up to 94%. The addition of these nanoparticles to the wastewater adsorbed all the dye and heavy metal elements. Ortashi et al. (2017) patented a method of preparing metal nanoparticles from fungi; the method includes the preparation of a biomass from fungal cells. The method was done by providing an aqueous solution, including a metal salt; mixing the biomass of fungal cells with the aqueous solution of metal salt; and incubating the resulting mixture at a temperature range of 35 °C to 60 °C to produce the metal nanoparticles. EL Badawi, Esawi and Ramadan (2014) invented an asymmetric composite membrane containing a polymeric matrix and carbon nanotubes within a single membrane layer. The carbon nanotubes are oriented within the polymeric matrix, and the composite membrane was formed by phase inversion. This invention was also related to a method for producing the composite membrane, which includes coating a surface with a film of a polymer solution containing a polymeric matrix, and carbon nanotubes dissolved in at least one solvent. The coated surface was immersed in a non-solvent to affect solvent and non-solvent demixing, resulting in phase inversion to form a carbon nanotube-containing membrane, and optionally removing the carbon nanotube-containing membrane from the surface. The invention was also related to a desalination method using the composite membrane.

1.5.2 Patents on Nanofibres for Its Applications in Desalination

Ensor et al. (2008) patented a filtration device together with a filtration medium having a plurality of nanofibres of diameters less than 1 micron formed into a fibre mat in the presence of an abruptly varying electric field. The filtration device consists of a support attached to the filtration medium and having openings for fluid flow therethrough. The device used for making a filter material was an electrospinning element configured to electrospin a plurality of fibres from a tip of the electrospinning element. A collector opposed to the electrospinning element was configured to collect electrospun fibres on a surface of the collector, and an electric field modulation device was configured to abruptly vary an electric field at the collector at least once during the electrospinning of the fibres. The method offers a support having openings for fluid flow and electrospins nanofibres across the whole openings. The invention abruptly varies an electric field at the collector at least once during the electrospinning of the fibres. Furthermore, the invention controls the electrospinning conditions in order to produce polymer nanofibres with an average fibre diameter of 100 nm and less. Nanofibres less than 200 nm have been found to improve the filtration properties of the resultant fibre. Kas et al. (2013) invented a composite liquid filtration platform together with a composite filtration medium featuring an electrospun polymeric nanofibre layer collected on a porous membrane. When in use, the porous membrane acted as a prefilter that was used in an upstream from the polymeric nanofibre layer to remove particles from a liquid stream flowing through the composite filtration structure. The nanofibre layer that was positioned downstream from the porous membrane was used as the retentive layer for critical filtration in order to provide biosafety assurance. The stage of the process is responsible for capturing microorganisms like bacteria, mycoplasma or viruses. The composite liquid filtration platform exhibited permeability advantages over conventional porous membranes or nanofibre mats spun on coarse non-wovens.

1.5.3 Companies in Collaboration with U.S. Patents

Apart from the innovation developed by researchers, companies in collaboration with U.S. patents have also developed novel nanotechnologies and improved the performance of existing technologies for wastewater treatment. In 2011, VeruTek technologies, Inc., received notice of U.S. patent allowance for environmental remediation and wastewater treatment product (Green-nano Zero valent iron). The product is a high-performing catalyst developed in collaboration with the U.S. Environmental Protection Agency. The product is ideal for a broad range of remediation applications, including treating produced water generated during oil and gas and other chemical production processes. green-nano zero-valent iron works more efficiently than conventional iron catalysts, significantly increasing the rate of oxidant activity, and it can be used under a wide range of conditions (Nanowerk 2011). Wetworks, a modular wastewater treatment plant, combines complete biological treatment via a moving bed bioreactor and U.S. patented nano-coated flat sheet ceramic membrane filtration, all packaged within a single international organisation for standardisation container for a superior wastewater treatment at reduced operating and maintenance costs. Wetworks is a reliable, efficient and highly cost-effective wastewater treatment, unlike traditional wastewater treatment systems (Wetworks 2013).

Furthermore, there are companies that have developed novel nanotechnologies for wastewater treatment. A Mexican company, Carbotecnia, specialises in the development and marketing of activated charcoal for the treatment of household water, in industry and commerce. The company offers high-tech equipment for water treatment using different techniques, including nanofiltration. Additionally, the company provides technical advice for equipment and treatment plant installation and other services (Carbotecnia 2014). Nano Sun in Singapore has been developing chemical and membrane-based water treatment technologies. They offer advanced industrial wastewater management solutions with an integrated, comprehensive and professional approach. Nano Sun incorporated various nanomaterials into membranes, which enable traditional membranes to possess multifunctional features such as anti-fouling through self-cleaning disinfection, degradation of organic pollutants and energy production (Nano Sun 2017).

1.6 Challenges

Literature on the benefits of nanotechnology has recently increased, but discussions on the potential effects of nanotechnology's extensive usage in consumer and industrial products is just beginning. There are challenges with the newness of nano-applications in the treatment of wastewater and with concerns regarding the potential impact of nanomaterials on health and the environment. Some extensive applications related to nanotechnology have an equally widespread potential to harmfully affect human health and the environment through the various exposure routes of nanoparticles (Curran et al. 2007) and occupational exposure (Boccuni et al. 2008). With the rapid rate of development in the area of nanotechnology and the attracting rate of publicity, concerns have been raised over the safety of nanomaterials in a variety of products. Granted that some alarms may not have been proven, the fact still remains that the toxicology of many nanomaterials has not yet been fully assessed. Existing data suggest that some nanomaterials can cause adverse health effects, but these data are too limited to draw conclusions (Tuccillo et al. 2011). Nonetheless, chemical residual that remains during wastewater treatment, forms a variety of known and unknown by-products, through reactions between the chemicals and some pollutants (Simate et al. 2012). Prolongedexposure to these by-products through the ingestion of drinking water, inhalation and body contact during regular indoor activities, such as: showering, bathing and cooking, may pose some cancer risks and non-cancer risks to human health. For instance, residual aluminium salts in treated water can result to Alzheimer's disease. Existing information on the toxicity of carbon nanotubes in drinking water is limited, with many open questions, despite their potential impact on human health and the environment, since carbon nanotubes have been receiving increasing attention (Acton 2012).

Nonetheless, the exceptional properties of nanomaterials have made them attractive for a substantial number of innovative, sustainable and green nanotechnology applications. In this regard, it is very vital that the scientific community, society and the industry take due advantage of nanotechnology prospects while overcoming its challenges. Nevertheless, not all innovatory changes are really sustainable, and a careful evaluation of the benefits that address the economic, social and environmental implications, together with the impact on occupational health and safety, is crucial (Bauer et al. 2008; Hutchison 2008). Particularly, the impact of nanotechnology on occupational health and safety should be carefully addressed. Addressing the impact should be done by putting into consideration the expected extensive use of nanotechnology and the likelihood of the subsequent increase of the exposure of nanomaterials in both living and occupational environments. Furthermore, obstacles in nano-manufacturing and handling and uncertainty regarding the stability of innovative nanotechnology under aggressive or long-term operation should be addressed. The lack of information with respect to the release and fate of nanomaterials in the environment, together with the limited knowledge concerning the nanomaterials' toxicological profile, further supports the need for a careful consideration of the health and safety risks associated with nanomaterial exposure (Lavicoli et al. 2014). In such a situation, responsible green nanotechnology development for wastewater treatment needs cautious consideration of the possible lifecycle impact of nanomaterials on health and the environment. Furthermore, ongoing investigations need to include the identification of the metrics to be used in toxicology studies and how to conduct experiments at environmentally relevant concentrations.

1.7 Conclusions

The objective of green nanotechnology in water treatment is to make use of the attractive physico-chemical and functional properties of nanomaterials that are energy-efficient, as well as economically and environmentally sustainable for treating wastewater. Nanotechnology will certainly play numerous roles in solving issues concerning the shortage of water and water quality in areas relevant to the treatment of water. The relevant areas include different separation processes and the reactive media for water filtration and the application of nanomaterials and nanoparticles in water disinfection and remediation. Thus, nanotechnology offers the potential to establish and develop water remediation processes in a better and more sustainable manner and eventually as close to a zero-emission approach as possible. While a lot of attention has been focused on the development and the potential benefits of nanomaterials in wastewater treatment processes, concerns have been raised with regard to their potential impact on human health and environmental toxicity. Nanotechnology can offer effective solutions to many pollution-related problems such as heavy metal contamination, the adverse effects of chemical pollutants, oil pollution, etc. If cautious consideration of the possible lifecycle impact of nanomaterials on health and the environment is taken into account, nanotechnology could provide eco-friendly alternatives for environmental management without harming the natural environment and, in turn, without harming human health. Thus, the process of nanotechnology transformation in the area of wastewater treatment depends mainly on safety and its sustainability in various applications of water treatment.

Acknowledgements The authors express their appreciation to Tshwane University of Technology, South Africa, and Covenant University, Nigeria. Appreciation also goes to the Department of Higher Education, South Africa. This chapter was supported by the Department of Higher Education, South Africa.

References

Abou-Gamra ZM, Ahmed MA (2015) TiO_2 nanoparticles for removal of malachite green dye from waste water. Adv Chem Eng Sci 5:373–388

Acton QA (2012) Advances in carbon research and applications, 2012 edition. Published by Scholarly Edition, Atlanta Georgia

Ahmaruzzaman M, Gupta VK (2011) Rice husk and its ash as low-cost adsorbents in water and wastewater treatment: a review. Ind Eng Chem Res 50(24):13589–13613

Ajayan PM (1999) Carbon nanotubes from carbon. Chem Rev 99(7):1787–1800

Alslaibi TM, Abustan I, Ahmad MA, Foul AA (2014) Preparation of activated carbon from olive stone waste: optimization study on the removal of Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Fe^{2+}, and Zn^{2+} from aqueous solution using response surface methodology. J Dispers Sci Technol 35(7):913–925

Alslaibi TM, Abustan I, Ahmad MA, Foul AA (2015) Comparative studies on the olive stone activated carbon adsorption of Zn^{2+}, Ni^{2+}, and Cd^{2+} from synthetic wastewater. Desalin Water Treat 54(1):166–177

Andriantsiferana C, Mohamed EF, Delmas H (2015) Sequential adsorption – photocatalytic oxidation process for wastewater treatment using a composite material TiO_2/activated carbon. Environ Eng Res 20(2):181–189

Anjum A, Lokeswari P, Kaur M, Datta M (2011) Removal of As(III) from aqueous solution using montmorillonite. J Chromatogr B 1:25–30

Anjum M, Miandad R, Waqas M, Gehany F, Barakat MA (2016) Remediation of wastewater using various nanomaterials: a review. Arab J Chem https://doi.org/10.1016/j.arabjc.2016.10.004

Ao Y, Xu J, Fu D, Shen X, Yuan C (2008) A novel magnetically separable composite photocatalyst: titania-coated magnetic activated carbon. Sep Purif Technol 61:436–441

Atieh MA, Bakather OY, Al-Tawbini B, Bukhari AA, Abuilaiwi FA, Fettouhi MB (2010) Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water. Bioinorg Chem Appl Article ID 603978:1–9

Ayub S, Khorasgani CF (2014) Adsorption process for wastewater treatment by using coconut Shell. Res J Chem Sci 4(12):1–8

Baalousha M (2009) Aggregation and disaggregation of iron oxide nanoparticles: influence of particle concentration, pH and natural organic matter. Sci Total Environ 407(6):2093–2101

Balamurugan R, Sundarrajan S, Ramakrishna S (2011) Recent trends in nanofibrous membranes and their suitability for air and water filtrations. Membranes 1:232–248

Baransi K, Dubowski Y, Sabbah I (2012) Synergetic effect between photocatalytic degradation and adsorption processes on the removal of phenolic compounds from olive mill wastewater. Water Res 46:789–798

Barry MC, Hristovski K, Westerhoff P (2014) Membrane fouling by vesicles and prevention through ozonation. Environ Sci Technol 48:7349–7356

Basiuk VA, Basiuk EV (eds) (2015) Green processes for nanotechnology, 1st edn. Springer, Mexico, p 434

Bauer C, Buchgeister J, Hischier R, Poganietz WR, Schebek L, Warsen J (2008) Towards a framework for life cycle thinking in the assessment of nanotechnology. J Clean Prod 16:910–926

Benn TM, Westerhoff P (2008) Nanoparticle silver released into water from commercially available sock fabrics. Environ Sci Technol 42:4133–4139

Bhatnagar A, Minicha AK (2006) Conventional and non-conventional adsorbents for removal of pollutants from water: a review. Indian J Chem Technol 13:203–217

Bhattacharya S, Saha I, Mukhopadhyay A (2013) Chatterjee D. role of nanotechnology in water treatment and purification: potential applications and implications. Int J Chem Sci Technol 3:59–64

Bina B, Amin M, Rashidi A, Pourzamani H (2012) Benzene and toluene removal by carbon nanotubes from aqueous solution. Arch Environ Prot 38(1):3–25

Blowes DW, Ptacek CJ, Benner SG, McRae CWT, Bennett TA, Puls RW (2000) Treatment of inorganic contaminants using permeable reactive barriers. J Contam Hydrol 45:123–137

Boccuni F, Rondinone B, Petyx C, Iavicoli S (2008) Potential occupational exposure to manufactured nanoparticles in Italy. J Clean Prod 16:949–956

Botes M, Cloete TE (2010) The potential of nanofibers and nanobiocides in water purification. Crit Rev Microbiol 36(1):68–81

Bt Fuadi NA, Ibrahim AS, Ismail KN (2012) Review study for activated carbon from palm shell used for treatment of waste water. J Purity Utility React Environ 1(5):252–266

Campelo JM, Luna D, Luque R, Marinas JS, Romero AA (2009) Sustainable preparation of supported metal nanoparticles and their applications in catalysis. A review. ChemSusChem 2 (1):18–45

Cao X, Ma J, Shi X, Ren Z (2006) Effect of TiO_2 nanoparticle size on the performance of PVDF membrane. Appl Surf Sci 253:2003–2010

Carbotecnia (2014) Nanofiltration. https://www.carbotecnia.info/encyclopedia/nanofiltracion/. Accessed 3 June 2018

Chantharawong P, Wongrueng A, Rakruam P, Wattanachira S, Takizawa S (2017) Effects of activated carbon and cationic exchange resin pretreatment on groundwater defluoridation by reverse osmosis process. Eng J 21(2):123–132

Chaturvedi S, Dave PN, Shah NK (2012) Applications of nanocatalyst in new era. J. Saudi Chem Soc 16:307–325

Chen W, Duan L, Zhu DQ (2007) Adsorption of polar and nonpolar organic chemicals to carbon nanotubes. Environ Sci Technol 41(24):8295–8300

Choi JH, Jegal J, Kim WN (2007) Modification of performances of various membranes using. MWNTs as a modifier. Macromol Symp 249:610–617

Cloete TE (2010) Nanotechnology in water treatment applications. Horizon Scientific Press, New York, p 196

Corry B (2008) Designing carbon nanotube membranes for efficient water desalination. J Phys Chem B112(5):1427–1434

Cortalezzi MM, Rose J, Barron AR, Wiesner MR (2002) Characteristics of ultrafiltration ceramic membranes derived from alumoxane nanoparticles. J Membr Sci 205:33–43

Curran MA, Frankl P, Heijungs R, Kohler A, Olsen SI (2007) Nanotechnology and life cycle assesment-A systems approach to nanotechnology and the environment. Woodrow Wilson Center for scholars, Washington, DC, p 2

Daniel SCGK, Malathi S, Balasubramanian S, Sivakumar M, Sironmani TA (2014) Multifunctional silver, copper and zero valent iron metallic nanoparticles for wastewater treatment. In book: application of nanotechnology in water research, chapter: 15. Inc., Editors: Dr. Ajay Kumar Mishra, Publisher: Wiley, pp 435–457

Das R, Ali ME, Hamid SBA, Ramakrishna S, Chowdhury ZZ (2014) Carbon nanotube membranes for water purification: a bright future in water desalination. Desal 336:97–109

Dave PN, Chopda LV (2014) Application of iron oxide nanomaterials for the removal of heavy metals: a review. J Nanotechnol Article ID 398569:1–14

de la Guardia M (2014) The challenges of green nanotechnology. Bioimpacts 4(1):1–2

de Velasquez MTO, Monje-Ramirez I, Paredes JFM (2013) Effect of ozone in UF-membrane flux and dissolved organic matter of secondary effluent. Ozone Sci Eng 35:208–216

Delmas H, Mohamed EF, Andriantsiferana C (2014) Photocatalytic degradation of an azo- dye on TiO_2 /activated carbon composite material. Environ Technol 35:355–363

DiGiano FA (2008) In pursuit of innovative membrane technology. In: IWA membrane research conference. Aug. 2008. University of Mass

Dobias J, Bernier-Latmani R (2008) Silver release from silver nanoparticles in natural waters. Environ Sci Technol 47(9):4140–4146

Dutta AK, Maji SK, Adhikary B (2014) C-Fe_2O_3 nanoparticles: an easily recoverable effective photo-catalyst for the degradation of rose bengal and methylene blue dyes in the waste-water treatment plant. Mater Res Bull 49:28–34

EL Badawi NAAH, Esawi and Ramadan (2014) Polymer-carbon nanotube nanocomposite porous membranes. Pub. No.: US 2014/0209539 A1:1–26

Elimelech E, Phillip WA (2011) The future of seawater desalination: energy, technology, and the environment. Science 333:712–717

Ensor DS, Walls HJ, Andrady A, Walker TA (2008) Particle filter system incorporating nanofibers Pub. No.: US 2008/0110342 A1:1-33

Feng Z, Qiu X, Haung R, Qiu X, Li M (2011) Removal of chromium in electroplating wastewater by nano-scale zero valent metal with synergistic effect of reduction and immobilization. Desalination 280:224–231

Fujishima A, Zhang XT, Tryk DA (2008) TiO_2 photocatalysis and related surface phenomena. Surf Sci Rep 63(12):515–582

Ge F, Le M-M, Ye H, Zhao BX (2012) Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymer-modified magnetic nanoparticles. J Hazard Mater 21:366–372

Geranio L, Heuberger M, Nowack B (2009) The behavior of silver nanotextiles during washing. Environ Sci Technol 43:8113–8118

Ghasemzadeh G, Momenpour M, Omidi F, Hosseini MR, Ahani M, Barzegari A (2014) Applications of nanomaterials in water treatment and environmental remediation. Front Environ Sci Eng 8(4):471–482

Girginova PI, Daniel-da-Silva AL, Lopes CB, Figueira P, Otero M, Amaral VS, Pereira E, Trindade T (2010) Silica coated magnetite particles for magnetic removal of Hg^{2+} from water. J Colloid Interface Sci 345(2):234–240

Girgis EA, Aziz CT (2013) The use of nano alloys in wastewater treatment. Pub. No: WO2013020564A2

Gotovac S, Yang CM, Hattori Y, Takahashi K, Kanoh H, Kaneko K (2007) Adsorption of polyaromatic hydrocarbons on single wall carbon nanotubes of different functionalities and diameters. J Colloid Interface Sci 314(1):18–24

Gottschalk F, Sonderer T, Scholz RW, Nowack B (2009) Modeled environmental concentrations of engineered nanomaterials (TiO_2, ZnO, Ag, CNT, fullerenes) for different regions. Environ Sci Technol 43:9216–9222

Greiner A, Wendorff J (2008) Functional self-assembled nanofibers by electrospinning. In: Self-assembled nanomaterials I. Springer, Berlin/Heidelberg, pp 107–171

Gu L, Chen Z, Sun C, Wei B, Yu X (2010) Photocatalytic degradation of 2,4-dichlorophenol using granular activated carbon supported TiO_2. Desalin 263:107–112

Gulyas H (2014) Solar heterogeneous photocatalytic oxidation for water and wastewater treatment: problems and challenges. J Adv Chem Eng 4(2):108–118

Gulyas H, Choromanski P, Muelling N, Furmanska M (2009) Toward chemical-free reclamation of biologically pretreated greywater: solar photocatalytic oxidation with powdered activated carbon. J Clean Prod 17:1223–1227

Gulyas H, Argáez ASO, Kong F, Jorge CL, Eggers S, Otterpohl R (2013) Combining activated carbon adsorption with heterogeneous photocatalytic oxidation: lack of synergy for biologically treated greywater and tetraethylene glycol dimethyl ether. Environ Technol 34(11):1393–1403

Gupta AK, Gupta M (2005) Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. Biomaterials 26(18):3995–4021

Gupta VK, Saleh TA (2013) Sorption of pollutants by porous carbon, carbon nanotubes and fullerene – an overview. Environ Sci Pollut Res 20:2828–2843

Gupta VK, Tyagi I, Sadegh H, Shahryari-Ghoshekand R, Makhlouf ASH, Maazinejad B (2015) Nanoparticles as adsorbent; a positive approach for removal of noxious metal ions: a review. Sci Technol Dev 34(3):195–214

Hansen LM, Smith DJ, Reneker DH, Kataphinan W (2005) Water absorption and mechanical properties of electrospun structured hydrogels. J Appl Polym Sci 95:427–434

Hashem EA (2014) Nanotechnology in water treatment, case study: Egypt. J Econ Dev Stud 2 (3):243–259

Hu H, Wang Z, Pan L (2010) Synthesis of monodisperse Fe_3O_4@silica core–shell microspheres and their application for removal of heavy metal ions from water. J Alloys Compd 492:656–661

Huang SH, Liao MH, Chen DH (2003) Direct binding and characterization of lipase onto magnetic nanoparticles. Biotechnol Prog 19(3):1095–1000

Huang Z-M, Zhang Y, Ramakrishna S, Lim C (2004) Electrospinning and mechanical characterization of gelatin nanofibers. Polymer 45:5361–5368

Hutchison JE (2008) Greener nanoscience: a proactive approach to advancing applications and reducing implications of nanotechnology. ACS Nano 2:395–402

Jaksi Z, Matovic J (2010) Functionalization of artificial freestanding composite nanomembranes. Dent Mater 3:165–200

Jang M, Chen W, Cannon F (2008) Preloading hydrous ferric oxide into granular activated carbon for arsenic removal. Environ Sci Technol 42:3369–3374

Jhansi SC, Campus MS, Mishra SK (2013) Wastewater treatment and reuse: sustainability options consilience. J Sustain Dev 10(1):1–15

Ji L, Chen W, Duan L, Zhu D (2009) Mechanisms for strong adsorption of tetracycline to carbon nanotubes: a comparative study using activated carbon and graphite as adsorbents. Environ Sci Technol 43:2322–2327

Jiana M, Liua B, Zhang G, Liua R, Zhang X (2015) Adsorptive removal of arsenic from aqueous solution by zeolitic imidazolate framework-8 (ZIF-8) nanoparticles. Colloids Surf A Physicochem Eng Asp 465:67–76

Jilílek T, Komárek M, Lederer T (2017) Polyurethane nanofiber membranes for waste water treatment by membrane distillation. J Nanotechnol 7143035:1–7

Jones CD, Fidalgo M, Wiesner MR, Barron AR (2001) Alumina ultrafiltration membranes derived from carboxylate-aluminoxane nanoparticles. J Membr Sci 193:175–184

Kadir AA, Puade Z (2013) The utilisation of aActivated Carbon (AC) from palm shell waste to treat textile wastewater. Adv Environ Biol 7(12):3621–3627

Kaegi R, Sinnet B, Zuleeg S, Hagendorfer H, Mueller E, Vonbank R, Boller M, Burkhardt M (2010) Release of silver nanoparticles from outdoor facades. Environ Pollut 158:2900–2905

Kanel SR, Manning B, Charlet L, Choi H (2005) Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. Environ Sci Technol 39:1291–1298

Kanel SR, Greneche JM, Choi H (2006) Arsenic(V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material. Environ Sci Technol 40:2045–2050

Karn BP, Bergeson LL (2009) Green nanotechnology: staddling promise and uncertainty. Nat Resour Environ 24:1–6

Kas OY, Kozlov M, Tkacik G, Nheim D, Goddard P, Leon SA (2013) Nanofiber containing composite membrane structures. Pub. No.: US 2013/0092622 A1:1-20

Kaushal A, Singh SK (2017) Removal of heavy metals by nanoadsorbents. A review. J Environ Biotechnol Res 6(1):96–104

Kaushik BK, Majumder MK (2015) Carbon nanotubes, properties and application. In: Carbon nanotube based VLSI interconnects, Analysis and design. Springer Briefs in Applied Sciences and Technology, New Delhi, p 17. https://doi.org/10.1007/978-81-322-2047-3_2

Khajeh M, Laurent S, Dastafkan K (2013) Nanoadsorbents: classification, preparation, and applications (with emphasis on aqueous media). Chem Rev 113(10):7728–7768

Khalkhali RA, Omidvari R (2005) Adsorption of mercuric ion from aqueous solutions using activated carbon. P J Environ Studies 14(2):185–188

Khan NA, Jung BK, Hasan Z, Jhung SH (2015) Adsorption and removal of phthalic acid and diethyl phthalate from water with zeolitic imidazolate and metal–organic frameworks. J Hazard Mater 282:194–200

Khedr MH, Omar AA, Abdel-Moaty SA (2006) Magnetic nanocomposites: preparation and characterization of co-ferrite nanoparticles. Colloids Surf A Physicochem Eng Asp 281:8–14

Kim J, Van der Bruggen B (2010) The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water treatment. Environ Pollut 158(7):2335–2349

Klink MJ, Ebenso EE, Crouch AD (2012) Physico-chemical characterization of different preparation routes of binary and ternary metal oxides on titanium substrates. Int J Electrochem Sci 7:3018–3030

Komolikov YI, Blaginina LA (2002) Technology of ceramic micro- and ultra-filtration members (review). Refract Ind Ceram 43:181–187

Kumar A, Gayakwad A, Nagale BD (2014) A review: Nano membrane and application. Int J Innovative Res Sci Eng Technol 3(1):8373–8381

Kumar SR, Jayavignesh V, Selvakumar R, Swaminathan K, Ponpandian N (2016) Facile synthesis of yeast cross-linked Fe_3O_4 nanoadsorbents for efficient removal of aquatic environment contaminated with As(V). Colloid Interface Sci 184:183–195

Kunduru KR, Nazarkovsky M, Farah S, Pawar RP, Basu A, Domb AJ (2017) Nanotechnology for water purification: applications of nanotechnology methods in wastewater treatment. In: Water purification: nanotechnology in the agri-food industry, vol 9. Academic, London, p 47

Kurian M, Nair DS (2015) Heterogeneous Fenton behavior of nano nickel zinc ferrite catalysts in the degradation of 4-chlorophenol from water under neutral conditions. J Water Process Eng 8:37–49

Kwak SY, Kim SH (2001) Hybrid organic/inorganic reverse osmosis (RO) membrane for bactericidal anti-fouling 1. Preparation and characterization of TiO_2 nanoparticle self- assembled aromatic polyamide thin-film-composite (TFC) membrane. Environ Sci Technol 35:2388–2394

Kyzas GZ, Matis KA (2015) Nanoadsorbents for pollutants removal: a review. J Mol Liq 203:159–168

Lavicoli I, Leso V, Ricciardi W, Hodson LL, Hoover MD (2014) Opportunities and challenges of nanotechnology in green economy. Environ Health 13(78):1–11

Lee K-J, Park H-D (2016) Effect of transmembrane pressure, linear velocity, and temperature on permeate water flux of high-density vertically aligned carbon nanotube membranes. Desalin Water Treat 57:26706–26717

Lee LY, Ng HY, Ong SL, Hu JY, Tao G, Kekre K, Viswanath B, Lay W, Seah H (2009) Ozone-biological activated carbon as a pretreatment process for reverse osmosis brine treatment and recovery. Water Res 43(16):3948–3955

Lehman SG, Adham S, Liu L (2008) Performance of new generation ceramic membranes using hybrid coagulation pretreatment. J Environ Eng Manage 18(4):257–260

Lenoble V, Bouras O, Deluchat V, Serpaud B, Bollinger J (2002) Arsenic adsorption onto pillared clays and iron oxides. J Colloid Interface Sci 225:52–58

Li D, Xia YN (2004) Electrospinning of nanofibers, reinventing the wheel? Adv Mater 16:1151–1170

Li Y, Wang S, Wei J, Zhang X, Xu C, Luan Z, Wu D, Wei B (2002) Lead adsorption on carbon nanotubes. Chem Phys Lett 357:263–266

Li Y-H, Ding J, Luan Z, Di Z, Zhu Y, Xu C, Wu D, Wei B (2003) Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes. Carbon 41:2787–2792

Lichtfouse E, Schwarzbauer J, Robert D (2012) Environmental chemistry for a sustainable. In: World: nanotechnology and health risks, vol 1. Springer Dordrecht, Heidelberg/London/New York, p 24

Lie W, Liu Y, Si X, Xu J, Du W, Yang J, Zhou T, Lin J (2017) Synthesis and magnetic properties of octahedral Fe_3O_4 via a one-pot hydrothermal route. Phys Lett A 381:314–318

Lim T-T, Yap P-S, Srinivasan M, Fane AG (2011) TiO_2 /AC composites for synergistic adsorption-photocatalysis processes: present challenges and further developments for water treatment and reclamation. Crit Rev Environ Sci Technol 41:1173–1230

Lin KYA, Chang HA (2015) Efficient adsorptive removal of humic acid from water using Zeolitic Imidazole Framework-8 (ZIF-8). Water Air Soil Pollut 226(2):1–17

Lin Y, Meziani M, Sun Y (2007) Functionalized carbon nanotubes for polymeric nanocomposites. J Mater Chem 17:1143–1148

Liu T, Zhao L, Sun D, Tan X (2010) Entrapment of nanoscale zero-valent iron in chitosan beads for hexavalent chromium removal from wastewater. J Hazard Mater 184:724–730

Liu Z, Wang H, Liu C, Jiang Y, Yu G, Mu X, Wang X (2012a) Magnetic cellulose-chitosan hydrogels prepared from ionic liquids as reusable adsorbent for removal of heavy metal ions. Chem Commun 48(59):7350–7352

Liu L, Liu J, Sun DD (2012b) Graphene oxide enwrapped Ag_3PO_4 composite: towards a highly efficient and stable visible-light-induced photocatalyst for water purification. Cat Sci Technol 2:2525–2532

Liua B, Jiana M, Liua R, Yaoc J, Zhang X (2015) Highly efficient removal of arsenic(III) from aqueous solution by zeolitic imidazolate frameworks with different morphology. Colloids Surfaces A Physicochem Eng Asp 481:358–366

Lu C, Chiu H (2006) Adsorption of zinc(II) from water with purified carbon nanotubes. Chem Eng Sci 61(4):1138–1145

Lu CS, Chiu H, Liu CT (2006) Removal of zinc(II) from aqueous solution by purified carbon nanotubes: kinetics and equilibrium studies. Ind Eng Chem Res 45(8):2850–2855

Lu H, Wang J, Stoller M, Wang T, Bao Y, Hao H (2016) An overview of nanomaterials for water and wastewater treatment. A review. Adv Mater Sci Eng Article ID 4964828:1–10

Luo T, Cui J, Hu S, Huang Y, Jing C (2010) Arsenic removal and recovery from copper smelting wastewater using TiO_2. Environ Sci Technol 44:9094–9098

Luo LH, Feng QM, Wang WQ, Zhang BL (2011) Fe_3O_4/Rectorite composite: preparation, characterization and absorption properties from contaminant contained in aqueous solution. Adv Mater Res 287:592–598

Ma X, Agarwal S (2016) Adsorption of emerging ionizable contaminants on carbon nanotubes: advancements and challenges. A review. Molecules 21:628–638

Ma H, Wang H, Na C (2015) Microwave-assisted optimization of platinum-nickel nanoalloys for catalytic water treatment. Appl Catal B Environ 163:198–204

Mahdavian AR, Mirrahimi MAS (2010) Efficient separation of heavy metal cations by anchoring polyacrylic acid on superparamagnetic magnetite nanoparticles through surface modification. Chem Eng J 159(1–3):264–271

Majeed S, Fierro D, Buhr K, Wind J, Du B, Boschetti-de-Fierro A, Abetz V (2012) Multi- walled carbon nanotubes (MWCNTs) mixed polyacrylonitrile (PAN) ultrafiltration membranes. J Membr Sci 403:101–109

Malik P (2004) Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. J Hazard Mater 113(1):81–88

Martínez-Huitle CA, Andrade LS (2011) Electrocatalysis in wastewater treatment: recent mechanism advances. Quim Nova 34(5):850–858

Masoud MS, El-Saraf WM, Abdel-Halim AM, Ali AE, Mohamed EA, Hasan HMI (2016) Rice husk and activated carbon for waste water treatment of El-Mex Bay, Alexandria Coast, Egypt. Arab J Chem 9:S1590–S1596

Matos J, Laine J, Herrmann JM, Uzcategui D, Brito JL (2007) Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenol photodegradation. Appl Catal B Environ 70:461–469

Matos J, Chovelon J-M, Cordero T, Ferronato C (2009) Influence of surface properties of activated carbon on photocatalytic activity of TiO_2 in 4-chlorophenol degradation. Open Environ Eng J 2:21–29

Matsumoto H, Tanioka A (2011) Functionality in electrospun nanofibrous membranes based on fiber's size, surface area, and molecular orientation. Membranes 1:249–264

Mauter MS, Wang Y, Okemgbo KC, Osuji CO, Giannelis EP, Elemelech M (2011) Antifouling ultrafiltration membranes via post-fabrication grafting of biocidal nanomaterials. ACS Appl Mater Interfaces 3(8):2861–2868

Maximous N, Nakhla G, Wan W, Wong K (2009) Preparation, characterization and performance of Al_2O_3/PES membrane for wastewater filtration. J Membr Sci 341(1):67–75

McCullagh C, Skillen N, Adams M, Robertson PKJ (2011) Photocatalytic reactors for environmental remediation: A review. J Chem Technol Biotechnol 86:1002–1017

Meng JH, Yang G, Yan L, Wang XY (2005) Synthesis and characterization of magnetic nanometer pigment Fe_3O_4. Dyes Pigments 66:109–113

Mintova S, Gilson J-P, Valtchev V (2013) Advances in nanosized zeolites. Nanoscale 5:6693–6703

Mohan D, Pittman CU Jr (2007) Arsenic removal from water/wastewater using adsorbents—A critical review. J Hazard Mater 142:1–53

Muga HE, Mihelcic JR (2008) Sustainability of wastewater treatment technologies. J Environ Manag 88:437–447

Nano Sun (2017) Your one stop solution for clean water supply. https://www.nanosun-main.com/. Assessed 3 June 2018

Nanowerk (2011) VeruTEK Receives U.S. patent notice of allowance for its Green-nano Zero valent iron catalyst. https://www.nanowerk.com/news/newsid=21754.php. Assessed 3 June 2018

Nicomel NR, Leus K, Folens K, Van Der Voort P, Liang GD (2016) Technologies for arsenic removal from water: current status and future perspectives. A review. Int J Environ Res Public Health 13962:1–24

Nowack B (2008) Pollution prevention and treatment using nanotechnology. In: Environmental aspects, vol 2. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, p 5

Oh JK, Park JM (2011) Iron oxide-based superparamagnetic polymeric nanomaterials: design, preparation, and biomedical application. Prog Polym Sci 36(1):168–189

Olvera RC, Silva SL, Robles-Belmont E, Lau EZ (2017) Review of nanotechnology value chain for water treatment applications in Mexico. Resour-Efficient Technol 3:1–11

Ortashi KMO, Awad MAG, Hendi AA, Abdelaziz ARM, Hendi ASA, Alahmed AA (2017) Synthesis of silver nanoparticles using fungi. Patent No: US 9,701,552 B1

Pal U, Sandoval A, Madrid SIU, Corro G, Sharma V, Mohanty P (2016) Mixed titanium, silicon, and aluminum oxide nanostructures as novel adsorbent for removal of rhodamine 6G and methylene blue as cationic dyes from aqueous solution. Chemosphere 163:142–152

Pan B, Lin D, Mashayekhi H, Xing B (2008) Adsorption and hysteresis of Bisphenol A and 17a-Ethinyl Estradiol on carbon nanomaterials. Environ Sci Technol 42(15):5480–5485

Pan S, Shen H, Xu Q, Luo J, Hu M (2012) Surface mercapto engineered magnetic Fe_3O_4 nanoadsorbent for the removal of mercury from aqueous solutions. J Colloid Interface Sci 365:204–212

Park KS, Ni Z, Côté AP, Choi JY, Huang R, Uribe-Romo FJ, Chae HK, O'Keeffe M, Yaghi OM (2006) Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. Proc Natl Acad Sci 103:10186–10191

Park SK, Park YG, Lim JL, Kim S (2015) Evaluation of ceramic membrane application for water treatment plants with a life cycle cost analysis. Desalin Water Treat 54(4):973–979

Pendergast MTM, Hoek EMV (2011) A review of water treatment membrane nanotechnologies. Energy Environ Sci 4:1946–1971

Peng Y, Liu H (2006) Effects of oxidation by hydrogen peroxide on the structures of multiwalled carbon nanotubes. Ind Eng Chem Res 45:6483–6488

Pholosi A, Ofamaja AE, Naidoo EB (2013) Effect of chemical extractants on the biosorptive properties of pine cone powder: influence on lead(II) removal mechanism. J Saudi Chem Soc 17:77–86

Qu X, Alvarez PJJ, Li Q (2013) Applications of nanotechnology in water and wastewater treatment. Water Res 47:3931–3946

Rahim M, Ng EP, Bakhtiari K, Vinciguerra M, Ali Ahmad H, Awala H, Mintova S, Daghighi M, Rostami FB, de Vries M, Motazacker MM, Peppelenbosch MP, Mahmoudi M, Rezaee F (2012) Zeolite nanoparticles for selective sorption of plasma proteins. Sci Rep 5:1–12

Rakhi MS, Suresh BG, Premalatha M (2016) Applications of nanotechnology in waste water treatment. A Review. Imp J Interdiscip Res 2(11):1500–1511

Rasheed MN (2013) Adsorption technique for the removal of organic pollutants from water and wastewater. In: Organic pollutants-monitoring, risk and treatment. Intech Publisher, Croatia, p 165

Reidy B, Haase A, Luch A, Dawson KA, Lynch I (2013) Mechanisms of silver nanoparticle release, transformation and toxicity. A Critical review of current knowledge and recommendations for future studies and applications. Materials 6:2295–2350

Rianjanu A, Kusumaatmaja A, Suyono EA, Triyana K (2018) Solvent vapor treatment improves mechanical strength of electrospun polyvinyl alcohol nanofibers. Heliyon 4(e00592):1–19

Richards HL, Baker PGL, Iwuoha E (2012) Metal nanoparticle modified Polysulfone membranes for use in wastewater treatment: A critical review. J Surf Eng Mater Adv Technol 2:183–193

Rickerby DG, Morrison M (2007) Nanotechnology and the environment: a European perspective. Sci Technol Adv Mater 8:19–24

Sadegh H, Shahryari-Ghoshekandi R, Kazemi M (2014) Study in synthesis and characterization of carbon nanotubes decorated by magnetic iron oxide nanoparticles. Int Nano Lett 4:129–135

Sadegh H, Ali GAM, Gupta VK, Makhlouf ASH, Shahryari-ghoshekandi R, Nadagouda MN, Sillanpää M, Megiel E (2017) The role of nanomaterials as effective adsorbents and their applications in wastewater treatment. J Nanostruct Chem 7:1–14

Sadeghi-Kiakhani M, Mokhtar Arami M, Gharanjig K (2013) Dye removal from colored-textile wastewater using chitosan-PPI dendrimer hybrid as a biopolymer: optimization, kinetic, and isotherm studies. J Appl Polym Sci 127:2607–2619

Sadiku O, Sadiku ER (2010) Numerical simulation for nanoparticle growth in flame reactor and control of nanoparticles. J Comput Theor Nanosci 7:1–9

Saien J (2010) Treatment of the refinery wastewater by nano particles of TiO_2. Pub. No.: US 2010/0200515 A1

Saito R, Fujita M, Dresselhaus G, Dresselhaus MS (1992) Electronic structure of chiral graphene tubules. Appl Phys Lett 60:2204-2206

Samanta HS, Das R, Bhattachajee C (2016) Influence of nanoparticles for wastewater treatment- a short review. Austin Chem Eng 3(3):1036–1042

Sanyasi S, Majhi RK, Kumar S, Mishra M, Ghosh A, Suar M, Satyam PV, Mohapatra H, Goswami C, Goswami L (2016) Polysaccharide-capped silver nanoparticles inhibit biofilm formation and eliminate multidrug-resistant bacteria by disrupting bacterial cytoskeleton with reduced cytotoxicity towards mammalian cells. Sci Rep 6(24929):1–16

Schwarzenbach RP, Egli T, Hofstetter TB, von Gunten U, Wehrli B (2010) Global water pollution and human health. Annu Rev Environ Resour 35:109–136

Seear K, Petersen A, Bowman D (2009) The social and economic impacts of nanotechnology: a literature review, Department of Innovation, Industry, Science and Research, Monash University, Australia, p, 67

Seitz F, Pollmann K, Mackenzie K, Opiolka S (2011) Photooxidation in combination with nanotechnologies – principles, developments and R&D approaches of an advanced technology for water and air treatment - Uviblox®. J Adv Oxid Technol 14:260–066

Sharma VK, Yngard RA, Lin Y (2009) Silver nanoparticles: green synthesis and their antimicrobial activities. Adv Colloid Interf Sci 145(1–2):83–96

Sheng Z, Van Nostrand JD, Zhou J, Liu Y (2015) The effects of silver nanoparticles on intact wastewater biofilms. Front Microbiol 6:1–11

Simate GS, Iyuke SE, Ndlovu S, Heydenrych M, Walubita LF (2012) Human health effects of residual carbon nanotubes and traditional water treatment chemicals in drinking water. Environ Int 39(1):38–49

Singh T, Pant K (2004) Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. Sep Purif Technol 36:139–147

Singh R, Singh S, Parihar P, Singh V, Prasad S (2015) Arsenic contamination, consequences and remediation techniques. A review. Ecotoxicol Environ Saf 112:247–270

Sironmani TA, Daniel SCGK (2011) Silver nanoparticles–universal multifunctional nanoparticles for bio sensing, imaging for diagnostics and targeted drug delivery for therapeutic applications. In: Dr. Izet Kapetanović (ed) Drug discovery and development– present and future. Intech publishers, Croatia, pp 463–488

Song H, Shao J, He Y, Liu B, Zhong X (2012) Natural organic matter removal and flux decline with PEG-TiO_2-doped PVDF membranes by integration of ultrafiltration with photocatalysis. J Membr Sci 405-406:48–56

Spahisa N, Addounb A, Mahmoudia H, Ghaffourc N (2008) Purification of water by activated carbon prepared from olive stones. Desalin 222:519–527

Stietiya MH, Wang JJ (2014) Zinc and cadmium adsorption to aluminium oxide nanoparticles affected by naturally occurring ligands. Environ Quality 43:498–506

Striolo A (2006) The mechanism of water diffusion in narrow carbon nanotubes. Nano Lett 6 (4):633–639

Stroeve P, Ileri N (2011) Biotechnical and other applications of nanoporous membranes. Trends Biotechnol 29(6):259–266

Susheela P, Radha R (2015) Production of activated carbon from dry coconut shell and its efficacy in treating waste water. Inter J Chem Biol Sci 1(10):1–9

Tansel B (2008) New technologies for water and wastewater treatment: a survey of recent patents. Recent Patents on Chem Eng 1:17–26

Tavallai H, Abdardideh D, Aalaei M, Zahmatkesh S (2012) New application of chemically modified multiwalled carbon nanotubes with thiosemicarbazide as a sorbent for separation and preconcentration of trace amounts of Co(II), Cd(II), Cu(II), and Zn(II) in environmental and biological samples prior to determination of flame atomic absorption spectrometry. J Chin Chem Soc 59:114–121

Teixido M, Pignatello JJ, Beltran JL, Grenados M, Peccia J (2011) Speciation of the ionizable antibiotic sulfamethazine on black carbon (biochar). Environ Sci Technol 45:10020–10027

Teja AS, Koh PY (2009) Synthesis, properties, and applications of magnetic iron oxide nanoparticles. Prog Cryst Growth Charact Mater 55(1–2):22–45

Thamilselvi V, Radha KV (2017) Silver nanoparticle loaded silica adsorbent for wastewater treatment. Korean J Chem Eng 34(6):1801–1812

Thangavel P, Sridevi G (2015) Green nanotechnology: the solution to sustainable development of environment. In: Environmental sustainability: role of green technologies. Springer, New Delhi, p 312

Theron J, Walker JA, Cloete TE (2008) Nanotechnology and water treatment: applications and emerging opportunities. Crit Rev Microbiol 34:43–69

Tong T, Elimelech M (2016) The global rise of zero liquid discharge for wastewater management: drivers, technologies, and future directions. Critical review. Environ Sci Technol 50:6846–6855

Tryba B, Morawski AW, Inagaki M (2003) Application of TiO_2 -mounted activated carbon to the removal of phenol from water. Appl Catal 41:427–433

Tuccillo ME, Boyd G, Dionysiou D, Shatkin JA (2011) Challenges and opportunity of nanomaterials in drinking water. Water Res Foundation, pp 1–4

Tung CH, Shen SY, Chang JH, Hsu YM, Lai YC (2013) Treatment of real printing wastewater with an electrocatalytic process. Sep Purif Technol 117(30):131–136

Valtchev V, Tosheva L (2013) Porous nanosized particles: preparation, properties, and applications. Chem Rev 113:6734–6760

Verma A, Tyagi S (2016) Biological synthesis of silver nanoparticles. Research & Reviews: J Pharm Nanotechnol 4:1–5

Verma A, Dwivedi R, Prasad R, Bartwal KS (2013) Microwave-assisted synthesis of mixed metal-oxide nanoparticles. J Nanoparticles 737831:1–11

Verma A, Sharma V, Tyagi S (2017) Green nanotechnology. Research and Reviews: J Pharm Pharm Sci 5(4):60–65

Visa M, Duta A (2013) TiO_2/fly ash novel substrate for simultaneous removal of heavy metals and surfactants. Chem Eng J 223:860–868

Visa M, Andronic L, Duta A (2015) Fly ash-TiO_2 nanocomposite material for multi- pollutants wastewater treatment. J Environ Manag 150:336–343

Voutchkov N (2017) Pretreatment for reverse osmosis desalination. Elsevier, Amsterdam, p 274

Walser T, Demou E, Lang DJ, Hellweg S (2011) Prospective environmental life cycle assessment of nanosilver t-shirts. Environ Sci Technol 45:4570–4578

Wang T (2007) Electrospun carbon nanofibers for electrochemical capacitor electrodes. PhD thesis, Georgia Institute of Technology, USA

Wang Y, Hsieh YL (2004) Enzyme immobilization to ultra-fine cellulose fibers via amphiphilic polyethylene glycol spacers. J Polym Sci A 42:4289–4299

Wang X, Chen X, Yoon K, Fang D, Hsiao BS, Chu B (2005) High flux filtration medium based on nanofibrous substrate with hydrophilic nanocomposite coating. Environ Sci Technol 39:7684–7691

Wang JP, Chen YZ, Feng HM, Zhang SJ, Yu HQ (2007) Removal of 2,4 – dichlorophenol from aqueous solution by static-air-activated carbon fibers. J Colloid Interface Sci 313:80–85

Wang X, Tao S, Xing B (2009) Sorption and competition of aromatic compounds and humic acid on multiwalled carbon nanotubes. Environ Sci Technol 43(16):6214–6219

Wang L, Zhu D, Duan L, Chen W (2010) Adsorption of single-ringed N- and S-hyterocyclic aromatics on carbon nanotubes. Carbon 48:3906–3915

Wang X, Guo Y, Yang L, Han M, Zhao J, Cheng X (2012) Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment. J Environ Anal Toxicol 2:2–7

Warner CL, Chouyyok W, Mackie KE, Niener D, Saraf LV, Drouby TC, Warner MG, Addleman RS (2012) Manganese doping of magnetic iron oxide nanoparticles: tailoring surface reactivity for a regenerable heavy metal sorbent. Langmuir 28(8):3931–3937

Wetworks (2013) Wetwork: the cleaner solution. https://iowapumpworks.com/images/2013/Wetworks_3D_Brochure.pdf. Assessed 3 June 2018

White BR, Stackhouse BT, Holcombe JA (2009) Magnetic γ-Fe_2O_3 nanoparticles coated with poly-L-cysteine for chelation of As(III), Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II). J Hazard Mater 161 (2):848–853

Wiesner MR, Barron AR, Jérôme R (2007) Membrane processes. In: Environmental nanotechnology: applications and impacts of nanomaterials. McGraw-Hill Companies, New York, p 356

Worch E (2012) Adsorption technology in water treatment: fundamentals, processes, and modeling. Walter de Gruyter GmbH & Co, Berlin/Boston, p 1

Wu H, Zhou W, Yildirim T (2007) Hydrogen storage in a prototypical zeolitic imidazolate framework-8. J Am Chem Soc 129:5314–5315

Wu YN, Zhou M, Zhang B, Wu B, Li J, Qiao J, Guan X, Li F (2014) Amino acid assisted templating synthesis of hierarchical zeolitic imidazolate framework-8 for efficient arsenate removal. Nanoscale 6:1105–1112

Xing W, Fan Y, Jin W (2013) Application of ceramic membranes in the treatment of water. In: Duke M, Zhao D, Semiat R (eds) Functional nanostructured materials and membranes for water treatment. Wiley-VCH Verlag GmbH & Co, KGaA, p 202

Xu J (2011) Synergy effect on a suspended mixture of ceria and activated carbon for the photocatalytic degradation of phenol. Powder Technol 210:1–5

Xu Q, Wei Y, Liu Y, Ji X, Yang L, Gu M (2009) Preparation of Mg/Fe spinel ferrite nanoparticles from Mg/Fe-LDH microcrystallites under mild conditions. Solid State Sci 11(2):472–478

Xu P, Zeng GM, Huang DL, Feng CL, Hu S, Zhao MH, Lai C, Wei Z, Huang C, Xie GX, Liu ZF (2012) Use of iron oxide nanomaterials in wastewater treatment: a review. Sci Total Environ 424:1–10

Yaacob WZW, Kamaruzaman N, Samsudin AR (2012) Development of nano-zero valent iron for the remediation of contaminated water. Chem Eng Trans 28:25–30

Yalcinkaya (2017) Mechanically enhanced electrospun nanofibers for wastewater treatment. E3S Web of Conferences 22:00193

Yanan Y, Huixuan Z, Peng W, Qingzhu Z, Jun L (2007) The influence of nano-sized TiO2 fillers on the morphologies and properties of PSF UF membrane. J Membr Sci 288(1):231–238

Yang K, Xing BS (2010) Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application. Chem Rev 110(10):5989–6008

Yang K, Wang X, Zhu L, Xing B (2006) Competitive sorption of Pyrene, Phenanthrene, and naphthalene on multiwalled carbon nanotubes. Environ Sci Technol 40(18):5804–5810

Yang K, Wu W, Jing Q, Zhu L (2008) Aqueous adsorption of aniline, phenol and their substitutes by multi-walled carbon nanotubes. Environ Sci Technol 42:7931–7936

Yang Y, Nie C, Deng Y, Cheng C, He C, Ma L, Zhao C (2016) Improved antifouling and antimicrobial efficiency of ultrafiltration membranes with functional carbon nanotubes. RSC Adv 6:88265–88276

Yao J, Bastiaansen CWM, Peijs T (2014) High strength and high modulus electrospun nanofibers. Fibers 2:158–186

Yin J, Zhu G, Deng B (2013) Multi-walled carbon nanotubes (MWNTs)/polysulfone (PSU) mixed matrix hollow fiber membranes for enhanced water treatment. J Membr Sci 437:237–248

Yu DG, Teng MY, Chou WL, Yang MC (2003) Characterization and inhibitory effect of antibacterial PAN-based hollow fiber loaded with silver nitrate. J Membr Sci 225:115–123

Zamora RMR, Schouwenaars R, Moreno AD, Buitrón G (2000) Production of activated carbon from petroleum cake and its application in water treatment for the removal of metals and phenol. Water Sci Technol 2(5):119–126

Zander NE, Gillan M, Sweetser D (2016) Recycled PET nanofibers for water filtration applications. Materials 9(247):1–10

Zare K, Gupta VN, Moradi O, Makhlouf ASB, Sillanpa M, Nadagouda MN, Sedehg H, Shahryari-Ghoshekandi R, Pal A, Wang ZJ, Tyagi I, Kazemi M (2015) A comparative study on the basis of adsorption capacity between CNTs and activated carbon as adsorbents for removal of noxious synthetic dyes: A review. J Nanostruct Chem 5:227–236

Zhang H (2013) Application of silver nanoparticles in drinking water purification. Doctoral thesis, University of Rhode Island

Zhang X, Zhou M, Lei L (2005) Preparation of photocatalytic TiO_2 coatings of nanosized particles on activated carbon by AP-MOCVD. Carbon 43:1700–1708

Zhang Q, Pan B, Pan B, Zhang W, Jia K, Zhang Q (2008) Selective sorption of lead, cadmium and zinc ions by a polymeric cation exchanger containing nano-Zr(HPO_3S)$_2$. Environ Sci Technol 42:4140–4145

Zhang S, Shao T, Bekaroglu SSK, Karanfil T (2009a) Adsorption of synthetic organic chemicals by carbon nanotubes: effects of background solution chemistry. Water Res 44(6):2067–2074

Zhang Q, Fan Y, Xu N (2009b) Effect of the surface properties on filtration performance of Al_2O_3eTiO_2composite membrane. Sep Purif Technol 66(2):306–312

Zhang SX, Niu HY, Hu ZJ, Cai YQ, Shi Y (2010a) Preparation of carbon coated Fe_3O_4 nanoparticles and their application for solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. J Chromatogr A 1217(29):4757–4764

Zhang W, Zuo L, Wang L (2010b) Visible-light assisted Methylene Blue (MB) removal by novel TiO_2/adsorbent nanocomposites. Water Sci Technol 61:2863–2871

Zhang S, Shao T, Karanfil T (2011a) The effects of dissolved natural organic matter on the adsorption of synthetic organic chemicals by activated carbons and carbon nanotubes. Water Res 45:1378–1386

Zhang D, Pan B, Wang B, Zhang H, Peng H, Ning P (2011b) Adsorption of sulfamethaxazole on functionalized carbon nanotubes as affected by cations and anions. Environ Pollut 159:2612–2621

Zhao X, Lv L, Pan B, Zhang W, Zhang S, Zhang Q (2011) Polymer-supported nanocomposites for environmental application. A review. Chem Eng J 170:381–394

Zhu A, Christofides PD, Cohen Y (2008) Effect of thermodynamic restriction on energy cost optimization of RO membrane water desalination. Ind Eng Chem Res 48(13):6010–6021

Zhu H, Jia Y, Wu X, Wang H (2009) Removal of arsenic from water by supported nano zero-valent iron on activated carbon. J Hazard Mater 172:1591–1596

Zodrow K, Brunet L, Mahendra S, Li D, Zhang A, Li Q, Alvarez PJJ (2009) Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal. Water Res 43(3):715–723

Chapter 2
Therapeutic Use of Inorganic Nanomaterials in Malignant Diseases

Andreea-Roxana Lupu, Traian Popescu, and Marko Stojanović

Contents

2.1 Introduction 49
2.2 Physicochemical Properties of Nanomaterials Which Influence Their Behavior in Biological Media 51
  2.2.1 Specific Surface Area 51
  2.2.2 The Zeta Potential 53
  2.2.3 The Hydrodynamic Size 55
  2.2.4 The “Biological Identity” of Nanomaterials 57
2.3 Behavior of Nanomaterials in Biological Media: Delivery and Cell Internalization 59
2.4 Current Applications of Nanomaterials in Cancer Therapies 62
  2.4.1 Passive Targeting 63
  2.4.2 Active Targeting 63
  2.4.3 The Use of Nanomaterials in Tumor Surgery 68
  2.4.4 Nanomaterial-Enhanced Radiotherapy 69
  2.4.5 Iron Replacement Therapy 70
  2.4.6 Antitumor Hyperthermia 70
  2.4.7 Photodynamic Therapy (PDT) 72
2.5 Discussion 74
References 77

A.-R. Lupu (✉)
Immunology Laboratory, “Cantacuzino” National Medico – Military Institute for Research and Development, Bucharest, Romania

Immunobiology Laboratory, Assay Development and Alternative Studies Department, “Victor Babes” National Research Institute of Pathology, Bucharest, Romania

T. Popescu
Laboratory of Atomic Structure and Defects in Advanced Materials, National Institute of Materials Physics, Magurele, Romania
e-mail: traian.popescu@infim.ro

M. Stojanović
Department of Pharmacology, Clinical Pharmacology and Toxicology, Faculty of Medicine, University of Belgrade, Belgrade, Serbia

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_2

Abstract Neoplastic disease has multifactorial etiology and insidious evolution which make it unlikely to be detected in early stages and very difficult to treat at later times. The effectiveness of standard therapeutic approaches is limited by severe adverse effects, metastasis, and tumor capacity to develop multidrug resistance.

The success of inorganic nanomaterial-based therapeutic agents depends on the degree to which these nanostructures satisfy general requirements for drug safety regarding biocompatibility, biodegradability, and stability and on their antitumor efficacy. Fabrication of such nanomedicines requires adequate assessment and engineering of nanomaterial physicochemical characteristics like particle size, specific surface area, surface charge, hydrodynamic size, and magnetic, optical, and photocatalytic properties. Together with surface functionalization and delivery method, these properties dictate the in vivo "biological identity" of the nanomaterial and its fate with respect to cellular uptake and distribution/accumulation inside the body.

We reviewed recent literature on interdisciplinary studies regarding applications of inorganic nanomaterials in the treatment of cancer. The major functions that inorganic nanomaterials can play in cancer therapy are:

1. Nanocarriers for therapeutic agents and active targeting ligands for molecules overexpressed on tumor tissues as well as for altered signal transduction pathways. Inorganic nanomaterial-based therapeutic agents are able to reduce tumor growth acting on neoplastic vasculature (by inhibiting angiogenesis, vasculogenesis, and vasculogenic mimicry) or on malignant cells (blocking activation of overexpressed receptors and their specific signaling pathways, inducing oxidative stress, and reducing multidrug resistance). Moreover, inorganic nanomaterials are able to inhibit tumor invasiveness and metastasis by reducing degradation of extracellular matrix, exosome secretion, and cell proliferation at the secondary site.
2. Contrast agents and medical adhesives in cancer surgery:
    - (i). Vital staining of sentinel lymph nodes (SLNs) where the first metastasis appears – the use of carbon nanoparticles, single-walled and multilayer carbon nanotubes, or superparamagnetic iron oxide nanoparticles was associated with a significantly higher number of harvested SLNs in breast and cervical tumors, lung cancer, papillary thyroid carcinoma, and prostate carcinoma.
    - (ii). Nanoparticle-based medical adhesives used for surgical wound closure – aqueous suspensions of iron oxide and silicon dioxide nanoparticles were shown to rapidly connect highly vascularized tissues (e.g., liver).
3. Inorganic sensitizers for radiotherapy – gold nanoparticles were reported to significantly enhance the efficiency of ionizing radiation and induce targeted cancer cell apoptosis, tumor growth inhibition, and increases of survival rates in tumor-bearing mice.
4. Antitumor agents based on specific material properties like surface plasmon resonance (photothermal heating), magnetic responsiveness (magnetic

hyperthermia), and photocatalysis (photodynamic therapy) – heat generated by plasmonic (gold-based) or magnetic (iron oxide-based) nanomaterials exposed to laser light or alternating magnetic fields, respectively, was shown to efficiently destroy tumors in mouse models or leads to promising results in clinical trials; the antitumor action of photoactivated TiO_2-based nanomedicines was assessed in numerous in vitro and several in vivo studies.

5. Adjuvant therapy (iron replacement therapy) – iron oxide colloids (IOC) are more efficient than free iron in treating iron-deficient anemia associated with cancer.

Overall, inorganic-organic therapeutic nanoplatforms provide enhanced treatment efficiency, reduced adverse effects, multiple antitumor action mechanisms, facile cell internalization, and diminished multidrug resistance.

Keywords Cancer · Inorganic nanomaterials · Targeted therapy · Nano-sized drug delivery system · Hyperthermia · Plasmonic photothermal therapy · Photodynamic therapy

2.1 Introduction

Cancer kills millions of people every year, and it is anticipated that the number of new cases will rise by about 70% over the next two decades (World Health Organization 2017). Considering the significant increase in the number of patients with malignant tumors and the economic burden that this condition carries for patients, health system, and society, as well as the negative emotional impact suffered by ill people due to unfavorable life expectancy prognosis, a breakthrough in the treatment and/or early diagnosis of cancer is greatly needed. In recent years, nanomaterials have become potential candidates for cancer therapeutics, various applications of different nanomaterials designed for the treatment of neoplastic diseases being currently under investigation in both laboratory and clinical practice.

Nanomaterials are defined as “a natural, incidental or manufactured material containing particles in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number-size distribution, one or more external dimensions is in the size range 1 nm–100 nm ” (Commission E 2011).

At present, by using versatile and inexpensive synthesis methods, a large variety of inorganic nanostructures (particles, rods, wires, tubes, plates, etc.) with different polymorphic structures, morphologies, and physicochemical properties can be obtained. Such synthesis- controlled properties, together with specific modifications (surface functionalization, drug conjugation), aimed to induce or enhance the therapeutic function of the inorganic nanomaterial and dictate the reactivity and behavior of the engineered nanostructure inside the human body (Fig. 2.1). The main prerequisites nanomaterials must have in order to be considered candidates for therapeutic applications are biocompatibility, biodegradability, stability, and minimal side effects (Marin et al. 2013; Solanki et al. 2008).

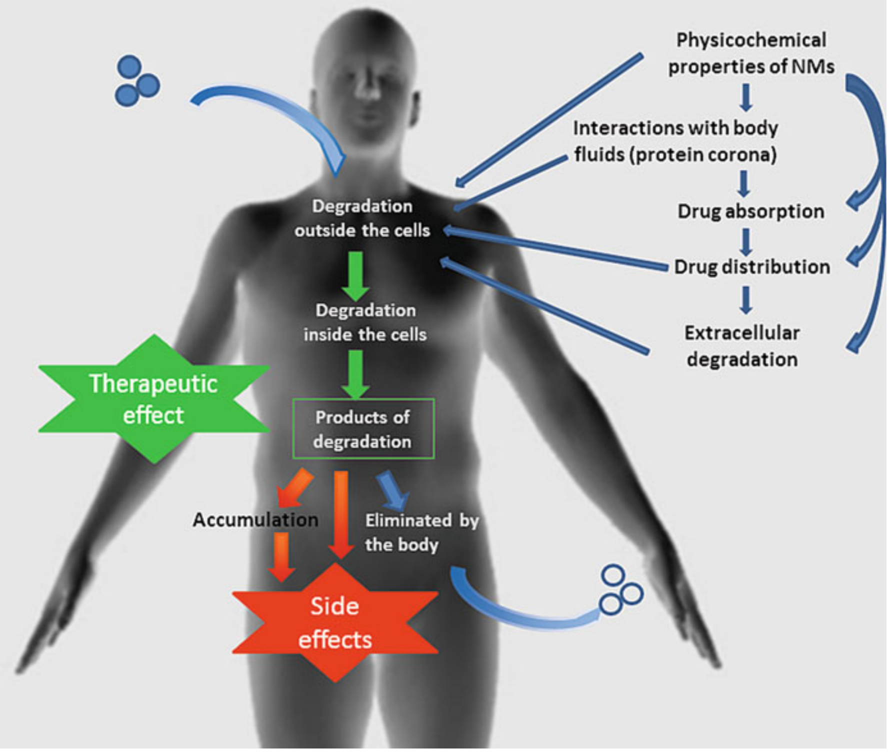


Fig 2.1 Nanomaterials' fate in the human body following systemic administration: in the biological fluids, based on their physicochemical properties, nanomaterials interact with endogenous proteins (forming protein corona) and/or are partially degraded and absorbed through digestive tract epithelium and blood vessel walls, being differentially distributed to body organs. After cell internalization, nanomaterials exert their biological role (therapeutic effect) followed by either accumulation in tissues and generation of side effects or elimination from the body through natural pathways

A biocompatible nanomaterial performs its therapeutic role without eliciting any undesirable local or systemic effects in the recipient patient (Williams 2008). When designing nanomaterials for therapeutics, both potential hemocompatibility and histocompatibility should be assessed (Li et al. 2012). Biocompatibility strongly relates to biodegradability – the characteristic of being decomposed by the living organism, leading to products of degradation that are nontoxic or are completely eliminated from the organism by natural metabolic pathways (Marin et al. 2013).

Stability refers to the capability of therapeutic nanomaterials to preserve their physicochemical properties and their biological activity for long term in the internal body environment (body fluids, gut mucosa, etc.). In vivo stability of nanomedicines is related to the requirement of no pre-release of drug (Zhang et al. 2014). For therapeutic efficacy, the active compound has to be released only after the nanostructure carrying it enters the target tumor cell.

In order to increase biocompatibility and ensure stability or to achieve targeted drug delivery (using nanoparticles as drug carriers), appropriate functionalization (chemical surface modification) of the used nanoparticles may be required. Functionalization is performed in order to protect both the carrier and the unstable drug molecules against degradation until the target organ and the target structure are reached (Marin et al. 2013; Solanki et al. 2008). The functionalized nanoparticle-drug system exhibits additional activity compared to drug alone, originated in specific material properties such as surface plasmon resonance (e.g., photothermal heating) (Ni et al. 2015; Huang and El-Sayed 2011), magnetic responsiveness (magnetic hyperthermia/targeting) (Khan et al. 2015; Reddy et al. 2012; Gubin 2009), and photocatalysis (Carp et al. 2004; Murakami et al. 2006; Hirakawa and Hirano 2006).

The condition of minimal side effects represents a constant target of all therapeutic approaches, including nanomedicine-based therapy. Accumulation of nanomaterials and their nonselective action (on both tumor and normal cells) can lead to tissue and cell lesions. In most cases, the metabolization of metallic nanomaterials will not lead to complete elimination of degradation products from the body. As an exception, inorganic iron is progressively incorporated in hemoglobin and eliminated from the body via natural pathways (Weissleder et al. 2014).

2.2 Physicochemical Properties of Nanomaterials Which Influence Their Behavior in Biological Media

The various biological effects induced by inorganic nanomaterials under in vitro or in vivo conditions are mediated by nonspecific and specific physicochemical interactions associated with volume and surface nanomaterial properties. Such important properties are particle size, specific surface area, surface charge, hydrodynamic size, and magnetic, optical, and photocatalytic properties.

2.2.1 *Specific Surface Area*

The biological reactivity of a nanomaterial is generally proportional to its specific surface area (surface area per unit mass of material). This area is determined based on the amount of gas substance adsorbed by a given amount of solid material. In general, the adsorption depends on the absolute temperature T, the pressure P, and the interaction potential E between the solid adsorbent and the adsorbate (Lowell et al. 2004). Under equilibrium temperature and pressure conditions, the weight W of gas adsorbed on a given amount of solid material can be written as

$$W = f(T, P, E) \tag{2.1}$$

This amount is generally determined at constant temperature, and thus, Eq. 2.1 may be simplified as

$$W = f(P, E) \tag{2.2}$$

By plotting the measured quantity W versus the chosen values of P at constant temperature, one obtains the adsorption isotherm of a particular gas-solid interface. The shape of such isotherms depends on the adsorption characteristics (e.g., the number of adsorbate layers formed at the gas-solid interface) and mechanism (chemisorption or physisorption).

With their theory, Stephen *B*runauer, Paul Hugh *E*mmett, and Edward *T*eller (BET) (1938) aimed to describe the physical adsorption of gas molecules on a solid surface. The BET theory represents an extension of the theory previously developed by Langmuir (valid for monolayer adsorption) to multilayer adsorption.

The proposed *BET adsorption isotherm* may be written as (Lowell et al. 2004)

$$\frac{1}{W(P/P_0 - 1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \tag{2.3}$$

The plot of $1/W(P/P_0 - 1)$ versus P/P_0 shows a linear behavior, usually for P in the range $0.05 < P/P_0 < 0.35$. The slope, s, and intercept, i, of this line are

$$s = \frac{C-1}{W_m C} \tag{2.4}$$

and

$$i = \frac{1}{W_m C} \tag{2.5}$$

By combining Eqs. 2.4 and 2.5, the weight of the monolayer W_m can be expressed as

$$W_m = \frac{1}{s+i} \tag{2.6}$$

while the BET constant C is given by

$$C = \frac{s}{i} + 1 \tag{2.7}$$

The total surface area S_t can be calculated based on the value of W_m resulted from Eq. 2.6.

$$S_t = \frac{W_m \overline{N} A_x}{\overline{M}} \tag{2.8}$$

where $\overline{N}$ is the Avogadro number and $\overline{M}$ and A_x are the molecular weight and cross-sectional area of the adsorbate, respectively. For nitrogen, the cross-sectional area is $A_x = 16.2$ Å.

The specific surface area is determined by dividing the total area S_t by the weight of the tested sample.

2.2.2 The Zeta Potential

Solid nanoparticles placed in liquid environments differentially adsorb ionic species from the liquid phase and acquire surface charge, an electrical potential being set up at the particle-electrolyte interface. The common term used to describe the occurrence of interfacial charge distribution is the electrical double layer (EDL).

The amount and type (positive or negative) of surface charge influence the cellular uptake and cytotoxicity of the charged nanomaterial (Eleonore Fröhlich 2012).

The amount of acquired charge is proportional to the average zeta potential of the studied nanomaterial. The zeta potential, ζ, is the electrostatic potential at the "shear plane" of a colloidal particle. In this context, the "shear plane" represents the interface between the ions strongly bound to the particle (moving along with the particle) and the bulk solution (loosely bound or unbound ions) Fig. 2.2.

Zeta potential is an important parameter characterizing the repulsive interactions between colloidal particles.

The zeta potential is frequently determined using the electrophoretic light scattering (ELS) method. The ELS is based on the analysis of the light scattered by charged particles that move in an electrolyte under the influence of an applied

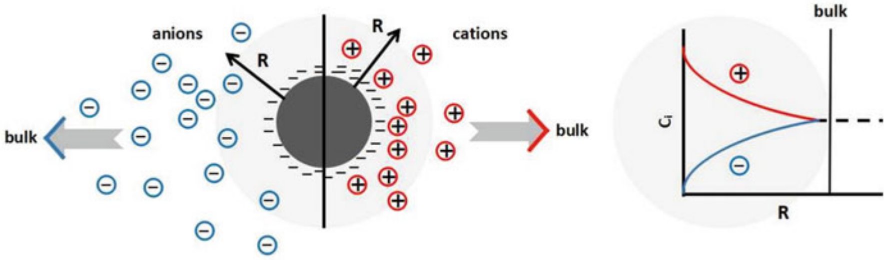


Fig. 2.2 Concentration of ions at the surface of a negatively charged nanoparticle and in the bulk electrolyte; (**a**) local depletion and accumulation of anions and cations, respectively, close to the surface; (**b**) the concentration C_i of ions of different species depends on the distance R from the NP surface. (Adapted from J. R. Soc. Interface 11: 20130931.https://doi.org/10.1098/rsif.2013.0931)

electric field. The constant velocity V_p of a charged particle subjected to an electric field of magnitude E is given by

$$V_p = \mu E \tag{2.9}$$

where the proportionality constant, μ, denotes the electrophoretic mobility. Usually, the velocities of such particles are very small, and it is convenient to express the mobility in terms of "mobility units," 1 M.U. = [10^{-4} cm^2/Vs].

An incident light beam with frequency v_0 is scattered by the moving particles at a frequency v_s, Doppler-shifted with respect to the incident frequency. The sign and magnitude of the Doppler shift depend on the velocity of the particle, the scattering angle, and the incident light wavelength in the suspension medium, according to Nicomp:

$$2\pi\Delta\nu = \mathbf{k}\cdot\mathbf{V_p} \tag{2.10}$$

where **k** is the scattering wave vector. The magnitude of **k** is given by

$$k = (4\pi n/\lambda_0) sin\theta/2 \tag{2.11}$$

where λ_0 denotes the wavelength of the incident beam in vacuum, n is the refractive index of the solution, and θ is the angle at which the scattered light is detected (Nicomp).

From Eq. 2.10 and 2.11 (using the definition of the scalar product), the Doppler shift $\Delta\nu$ can be expressed as

$$\Delta\nu = \left(kV_p/2\pi\right)cos(\theta/2) = \left(2nV_p/\lambda_0\right)sin(\theta/2)cos(\theta/2) = \left(nV_p/\lambda_0\right)sin\theta \tag{2.12}$$

By substituting the expression of the particle velocity from Eq. 2.9, the electrophoretic mobility, μ, can be written as

$$\mu = (\lambda_0/nsin\theta)(1/E)\Delta\nu \tag{2.13}$$

The mean zeta potential, ζ, is linearly related to the mobility μ, when the thickness of the electric double layer (EDL), ${\lambda_D}^{-1}$, is small compared to the mean diameter, R, of the particles (Smoluchowski approximation) ($\lambda_D R \gg 1$). In this case,

$$\xi = \eta\mu/\varepsilon \tag{2.14}$$

where η and μ represent the viscosity and the dielectric constant of the solvent, respectively.

In cases when ${\lambda_D}^{-1}$ is large compared to the mean diameter, R, of the particles (Hückel limit approximation) ($\lambda_D R << 1$), the zeta potential is given by

$$\xi = \frac{3}{2}\eta\mu/\varepsilon \tag{2.15}$$

The Debye length λ_D increases with the ionic strength of the solution.

2.2.3 The Hydrodynamic Size

When a particle moves in a fluid, such as blood flow, either under the influence of an applied force or due to Brownian motion, it is subjected to frictional forces. The frictional force $\mathbf{F}_\mathrm{f}$ is proportional to the velocity, $\mathbf{v}$, of the particle

$$\mathbf{F}_\mathrm{f} = -f\mathbf{v} \tag{2.16}$$

the proportionality constant f denoting the frictional coefficient. The minus sign shows the opposite directions of vectors $\mathbf{F}_\mathrm{f}$ and $\mathbf{v}$ (the frictional force opposes the motion of the particle).

For a sphere of radius R, the frictional coefficient depends on the viscosity of the fluid according to Stokes's law (Schuster 2000):

$$f = 6\pi\eta R \tag{2.17}$$

where η is the viscosity coefficient.

In case of Brownian motion, the diffusion coefficient D can be expressed in terms of the frictional coefficient f according to Einstein's relation (Schuster 2000):

$$D = \frac{k_B T}{f} \tag{2.18}$$

or, using Eq. 2.17

$$D = \frac{k_B T}{6\pi\eta R} \tag{2.19}$$

If the diffusion coefficient is known, based on Eq. 2.19, the hydrodynamic radius R_H (Einstein-Stokes radius) can be calculated from

$$R_H = R = \frac{k_B T}{6\pi\eta D} \tag{2.20}$$

Thus, R_H represents the radius of a sphere with the same diffusion coefficient as the studied particle (Fig. 2.3).

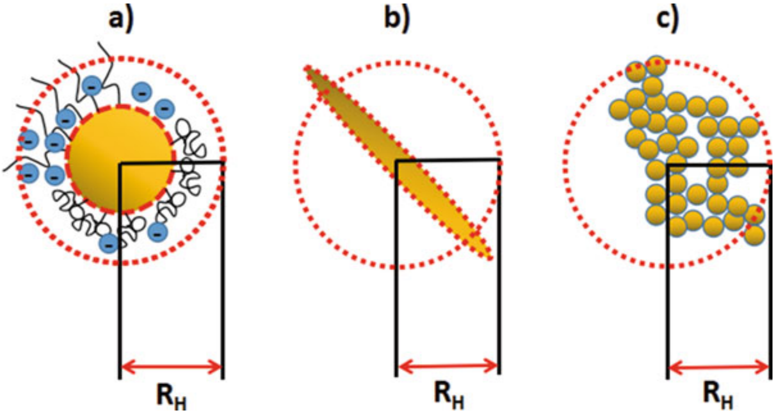


Fig. 2.3 Schematic illustration of the hydrodynamic radius, R_H, for (**a**) nanoparticle (yellow) with adsorbed/bound ions, folded and unfolded proteins on its surface; (**b**) elongated nanoparticle; (**c**) nanoparticle agglomerate

The diffusion coefficient is related to the mean-square distance $\langle r^2 \rangle$diffused by the particle in time t by (derived from Fick's law (Schuster 2000):

$$\langle r^2 \rangle = 6Dt \tag{2.21}$$

Thus, the diffusion coefficient may in principle be determined by analyzing the motion of Brownian particles.

The dynamic light scattering (DLS) method is frequently used for this purpose. In DLS, an incident laser beam is scattered by a volume of particles in Brownian motion. While the scattering particles change their positions, the electric field $E_s(t)$ and intensity $I_s(t) = |E_s(t)|^2$ of the scattered light fluctuate with time (Schuster 2000). The autocorrelation function $g_2(t)$ of the photocurrent resulting from the fluctuating intensity of the scattered light is (Berne and Pecora 1976)

$$g_2(t) = 1 + \beta e^{-2q^2Dt}, \tag{2.22}$$

where β is an instrumental constant and q is the magnitude of the scattering vector, $(4\pi n/\lambda_0)\sin(\theta/2)$, where n is the refractive index of the solvent, λ_0 is the wavelength of the incident light in vacuum, and θ is the scattering angle. Eq. 2.22 leads to

$$ln(g_2 - 1) = 1 - 2q^2Dt. \tag{2.23}$$

The slope of the semilogarithmic plot resulted from Eq. 2.23 is $(-2q^2D)$. Since q^2 is known, the diffusion coefficient D can be calculated from this slope.

The hydrodynamic radius is increased when nanomaterials enter the blood flow due to adsorption of plasma proteins on their surface. This hydrodynamic enlargement and biochemical surface modification influences the in vivo behavior of nanomaterials.

2.2.4 The "Biological Identity" of Nanomaterials

The nanomaterial - target cell interaction is only in rare cases directly influenced by the physicochemical properties of the nanomaterials. Under in vivo environments nanomaterials undergo modifications well before they reach their target cells. The overall induced modifications define a nanomaterial state called the "biological identity" of the nanomaterial which dictates its biological behavior and effects. The always present and most important modification is the covering of nanomaterial surfaces with bound and adsorbed proteins which form the so-called protein corona. Uncontrolled protein adsorption may reduce the targeting capacity and promote the clearance from the bloodstream of therapeutic nanomaterials. On the other hand, by functionalizing nanomaterials with chosen proteins or by engineering their surface to selectively adsorb specific endogenous proteins, improved nanomedicines could be obtained (Nguyen and Lee 2017; Caracciolo et al. 2017).

In this chapter, we briefly mention several of the characteristics of the protein corona and its importance in nanomaterial-based antitumor therapy.

The structure of the protein corona depends on the nature of the biochemical or physiological environments (blood, interstitial fluid, cell culture medium, cell cytoplasm, etc.), the duration of exposure, and the physicochemical properties (size, shape, composition, surface functional groups, and surface charges) of the involved nanomaterials (Rahman et al. 2013). The protein corona generally consists of two regions: the "hard corona" (strongly bound proteins that interact directly with the nanomaterial surface) and the "soft corona" (proteins that weakly interact with the hard corona by means of protein-protein interactions) (Monopoli et al. 2011). The formation of protein corona is a dynamical process which may be considered to occur in two stages (not clearly separated thought). In the early stage, proteins with the highest concentration are quickly adsorbed on the surface of the exposed nanomaterials. Over time, however, during the late stage, these proteins are desorbed and replaced with proteins of higher and more specific physicochemical affinity for the given material (Vroman effect (Vroman et al. 1980)). The adsorption of proteins does not however completely mask the surface of nanoparticles or their functional groups (Rahman et al. 2013; Aggarwal et al. 2009; Simberg et al. 2009).

Parameters Affecting the Protein Corona

The characteristics of the protein corona (structure, composition, thickness, conformation) depend on a variety of nanomaterial properties (size, shape, curvature, surface charge, solubility, hydrophobicity, surface modifications etc.) (Rahman et al. 2013; Lynch and Dawson 2008; Lundqvist et al. 2011; Mahmoudi et al. 2011), among which hydrophobicity and surface charge proved to be more relevant than other parameters (Aggarwal et al. 2009).

Effects of Surface Charge

Concerning the role of the surface charge, reports indicate a direct proportionality between the surface charge and the protein adsorption (Rahman et al. 2013). Besides influencing the protein adsorption rates, surface charge may also induce alterations in the protein conformation (Rahman et al. 2013). Regarding the role of the charge type, positively charged nanoparticles preferentially adsorb proteins with isoelectric points $IP < 5.5$, while negatively charged nanomaterials show higher affinity for proteins with $IP > 5.5$ (Aggarwal et al. 2009).

Effects of Hydrophobicity

Similar effects have been related to the hydrophobicity of the studied nanomaterials, hydrophobic surfaces being proved to adsorb higher amounts of proteins and induce stronger protein denaturation compared to hydrophilic surfaces, as well as to affect the composition of the protein corona (Aggarwal et al. 2009; Cedervall et al. 2007).

Effects of Nanoparticle Size and Curvature

The higher specific surface area associated with smaller nanoparticles leads to an increased protein adsorption rate, inversely proportional to the particle size. Besides protein-binding rate, another parameter found to depend on the particle size (when considering the same type of material) is the composition of the protein corona (Lundqvist et al. 2011; Gessner et al. 2000). The dependence of the protein corona composition and structure on the nanoparticle size becomes stronger as the particle size approaches the size of the folded proteins (Rahman et al. 2013).

Regarding the effects of particle surface curvature, proteins adsorbed to highly curved surfaces maintain their conformation better than those adsorbed to less curved surfaces (Rahman et al. 2013).

2.3 Behavior of Nanomaterials in Biological Media: Delivery and Cell Internalization

Inorganic nanomaterials are suitable for both local and systemic deliveries (Li et al. 2012). Local delivery (inhalation, topical administration, etc.) has the advantage of being noninvasive and induces less severe adverse effects in the treated patients. Inhaled drugs are localized to the target organs, and the required therapeutic doses are generally lower in this case compared to systemic delivery (Rau 2005). In an attempt to prolong the pulmonary residence time, inhaled nanomedicines were designed to adhere to airway mucus. Using a mouse model, Schneider et al. have recently shown, however, that smaller particles that avoid mucoadhesion and pass through the mucus barrier are more efficient than mucoadherent ones (which could be, at least in part, eliminated by physiologic mucus clearance mechanisms (Schneider et al. 2017). Inhaled nanomaterials are rapidly taken up by lung macrophages, leading to inflammation (Donaldson et al. 2013). High doses of inhaled nanomedicines may lead to adverse effects, including an increased risk of cardiovascular disease (Gerloff et al. 2017).

In the case of topical (transdermal) delivery, it is necessary that the used nanomaterials have affinity for both lipophilic and hydrophilic phases, and they do not induce irritation at the administration site (Uchechi et al. 2014). A wide range of nanomaterials including magnetic nanoparticles, quantum dots, titanium and zinc oxides, carbon nanotubes, and fullerenes are suitable for transdermal delivery, their potential skin sites for targeting being stratum corneum, furrows, and hair follicles (Larrañeta et al. 2016).

Having access to almost all parts of the body, systemic delivery (intravenous or oral administration) is widely used in clinical care. In the case of therapeutic nanomaterials, however, systemic delivery can lead to severe side effects due to accumulation of inorganic nanomaterials in vital organs, other than the injured ones. As targeted antitumor therapy aims to localize and maximize the effect in neoplastic tissues and to reduce/eliminate the damage to normal tissues, local and topical administration seems to be a better option for nanomaterial-based treatment of cancer diseases. Systemic delivery is still preferred when the target organs are difficult to reach by drug molecules (e.g., brain) and when the used inorganic nanoparticles can be guided (using magnetic fields or based on specific antibody-receptor interactions) toward the tumor tissue.

Intravenous delivery of drugs, including therapeutic nanomaterials, is usually associated with a quick response. Since high systemic doses are needed in order to obtain a beneficial effect in the affected organ, toxicity is often associated with intravenous administration (Verma et al. 2010).

In the blood flow, nanomaterials are either internalized by monocytes that further accumulate in inflamed tissues (including tumors) or, most of them, leave the blood vessels and enter tissues where they are engulfed by resident macrophages (Lowell et al. 2004).

Following intravenous administration, the distribution of nanomaterials in the body depends not only on their physicochemical properties but also on the site of injection into the blood flow. Nanomaterials injected in the central component of the blood flow will go to well-perfused organs, such as the heart, liver, and kidney, while nanomaterials from peripheral component will reach adipose tissue and skeletal muscle. Only few nanomaterials will reach organs protected by anatomic barriers (e.g., spinal cord) or characterized by reduced blood flow (e.g., joints or middle ear fluid) (Singh 2015). For an efficient treatment of these organs, local administration of therapeutic nanomaterials is required. Moreover, nanomaterial extravasation and spreading in body tissues is increased in fenestrated blood vessels present in normal organs (spleen, liver, kidneys, etc.) but also in tumors (Wang et al. 2012a),

Oral administration is noninvasive, but sometimes, it can be inefficient due to the degradation of therapeutic nanomaterials in the gastrointestinal tract and/or limited absorption (Uchechi et al. 2014; Esipova et al. 2012). Prior to intestinal uptake, ingested nanomaterials pass through different pH environments (from pH ≈ 6.6 in the oral cavity to pH ≈ 2 in the stomach). This affects the net surface charge and solubility of nanomaterials and subsequently their agglomeration and cellular uptake (Schneider et al. 2017; Singh 2015; Fröhlich and Roblegg 2012). Similar to inhalation, oral delivery of non-mucoadhesive nanomaterials is associated with enhanced particle distribution and drug delivery (Maisel et al. 2015). In some cases, oral administration of therapeutic nanomaterials can be associated with major adverse effects such as hepatitis and liver fibrosis (Schneider et al. 2017), lesions of gastrointestinal tract (Winkler et al. 2016), accumulation in vital organs like the brain and heart (Yildirimer et al. 2011; Saraiva et al. 2016), autoimmune-related toxicity (Sharma et al. 2013), etc.

The uptake of nanomaterials in neoplastic tissue depends on:

- The physicochemical properties of nanomaterials. For example, size and shape are critical for margination of nanomaterials in blood vessels, interaction with cell membranes (binding avidity of nanomaterials to molecular targets of interest), and drug release (Toy et al. 2014).
- The structure and type of tumor. The varying uptake rates of nanomaterials in tumors are a direct consequence of structural and pathological heterogeneity of different cancers (Lowell et al. 2004; Saraiva et al. 2016). Moreover, the fact that a specific tumor presents heterogeneous distribution of different tumor cell types and corresponding vasculature explains the preferential accumulation of nanomaterials in certain tumor zones when compared with other ones (Senger et al., 1983). Tumor blood vessels have a leaky structure and are highly permeable. Moreover, the lymphatic drainage is inefficient. These structural and functional particularities of tumors allow and promote accumulation of nanomaterials in neoplastic tissues (Zhang et al. 2014; Sharma et al. 2013). To reach the tumor tissue and exert their therapeutic role, nanomaterials needs to migrate toward blood vessel walls (margination, radial drift) (Saraiva et al. 2016), and this process is significantly influenced by particle size, density, and shape (Toy et al. 2011; Müller et al. 2014).

- The number and the activation state of infiltrated macrophages. Tumor mass is characterized by an abnormally higher cell density (cell number/unit of space) compared with the corresponding healthy organ (Norton and Massagué 2006). This explains, in part, the higher number of macrophages relative to normal tissue. The main reason, however, for a significantly increased number of macrophages in the tumor mass compared with healthy tissue is that during cancer development, macrophages are co-opted by neoplastic transformed cells to enhance cell proliferation and invasiveness (Weissleder et al. 2014; Liu and Cao 2015). Moreover, tumor-associated macrophages (TAM) act as a proinflammatory component of the immune system and create a pro-tumorigenic microenvironment (Bussard et al. 2016). As TAM recruitment is more pronounced in invasive regions of the tumors, it is plausible that nanomaterials tend to preferentially accumulate in the peripheral cancer tissues (Weissleder et al. 2014).

Understanding the mechanisms of nanomaterial internalization in cells is still a challenge due to the huge variability of chemical and physical properties of nanomaterials. In some cases, nanomaterials (e.g., iron oxide nanoparticles) can temporarily bind to the external membrane and interfere with cell surface mechanism, but they do not influence cell viability (Bulte and Kraitchman 2004).

The characteristics of nanoparticles (especially size) influence their cellular uptake mechanism (Doherty and McMahon 2009). Modifying the surface of nanomaterials with polymers (e.g., dextran, PEG) promotes nonspecific cellular uptake of nanomaterials by preventing aggregation, enhancing stability and solubility (Solanki et al. 2008; Bulte and Kraitchman 2004; Zhang et al. 2011a).

It is considered that nanomaterials with particle sizes beyond 0.5 μm are recognized as foreign structures and engulfed by specialized phagocytic cells, especially macrophages, but also monocytes, neutrophils, and dendritic cells (Weissleder et al. 2014; Groves et al. 2008). However, the main mechanism used by cells to internalize nanomaterials is not phagocytosis, but macropinocytosis (Geiser et al. 2005; Kuhn et al. 2014).

The binding of nanomaterials to target cellular receptors is followed by rearrangement of these receptors in the plasma membrane (usually receptor clustering occurs) and receptor-mediated endocytosis. Thus, the mechanism of nanomaterials internalization depends on both the coating molecules and the endocytosis of specific target receptor (Toy et al. 2014). Cross-linked dextran iron oxide nanoparticles (CLIOs) are capable to enter the cells through lectin receptor-mediated macropinocytosis (Weissleder et al. 2014), while SPIONs (superparamagnetic iron oxide nanoparticles) can be internalized by passive mechanisms, phagocytosis, micropinocytosis, and clathrin-mediated or receptor-mediated endocytosis (Wimpenny et al. 2012).

Due to their small size and to the fact that the membrane permeability is higher in tumor cells than in normal cells, nanomaterials preferentially accumulate in cancer cells (Anshup et al. 2005; Haltiwanger 2014).

Following their internalization by either macropinocytosis or phagocytosis, nanomaterials are encapsulated in lysosome and degraded by lysosomal enzymes and acids (Weissleder et al. 2014). Degradation products of nanomaterials can induce lysosomal disruption, oxidative stress, and release of proapoptotic proteins and proinflammatory mediators (Weissleder et al. 2014).

Moreover, some nanomaterials (e.g., TiO_2 and silver nanoparticles) are deposited at the cell surface or inside organelles and produce high amounts of reactive oxygen species (ROS) (directly or indirectly – by activating cellular signaling pathways), leading to oxidative stress (Manke et al. 2013). Cellular ROS production and mitochondrial damage amplify each other, leading to cell apoptosis and inflammation (Gerloff et al. 2017; Manke et al. 2013). For example, internalized by immune cells, SiO_2 (both crystalline and amorphous) and TiO_2 nanomaterials induce inflammasome activation followed by oxidative stress, release of proinflammatory cytokines, and ultimately cell death (Winter et al. 2011; Kojima et al. 2014).

Oxidative stress induced by nanomaterials represents one of the main mechanisms responsible for both anticancer effect and harmful effects associated with nanomaterials (Manke et al. 2013; Nel et al. 2006; Fujiwara et al. 2015).

2.4 Current Applications of Nanomaterials in Cancer Therapies

Neoplastic disease has multifactorial etiology and insidious evolution which make it unlikely to be detected in early stages and very difficult to treat at later times. Tumor expansion and metastasis are associated with breakdown of the immune response and development of multidrug resistance. New therapeutic agents and delivery strategies characterized by increased and targeted antitumor action are needed in order to efficiently destroy tumor cells without significantly affecting the surrounding normal tissue.

The main applicability of nanomaterials in cancer therapy is represented by nanomedicines – therapeutic nanostructures in which nanomaterials act as nanocarriers and/or active antitumor agents by themselves.

Inorganic nanomaterials with controlled shapes and sizes can be synthesized by facile and inexpensive methods and functionalized for therapeutic applications. Moreover, most metallic nanoparticles can be tracked inside the body using imaging techniques (e.g., magnetic resonance imaging (MRI) (Saraiva et al. 2016). Based on their composition and physicochemical properties, as well as the antitumor, targeting, or tracking agents they carry on their surface, functionalized inorganic nanomaterials form multifunctional anticancer therapeutic nanoplatforms. Such nanoplatforms are used for targeted drug delivery and/or antitumor action based on material properties like plasmon resonance (e.g., photothermal heating), magnetic responsiveness (magnetic hyperthermia/targeting), and photocatalysis (photodynamic therapy) (Ni et al. 2015; Huang and El-Sayed 2011; Khan et al. 2015;

Reddy et al. 2012; Gubin 2009; Carp et al. 2004; Murakami et al. 2006; Hirakawa and Hirano 2006).

With respect to the way in which nanomaterials (functionalized or not) reach the tumor mass, accumulate, and exert their effects, the nanomedicine-based therapy can be classified into untargeted therapy (passive targeting) and targeted therapy (active targeting). Furthermore, depending on the addressed structure (tumor vascular bed or cancer cells), active targeting can be split into vascular targeting and tumor targeting (Zhang et al. 2014; Farokhzad and Langer 2009).

2.4.1 Passive Targeting

Passive targeting is independent of the characteristics of cancer cells. Therapeutic nanomaterials are driven by the blood flow to the tumor mass where the leaky vasculature allows their extravasation and diffusion in the neoplastic tissue. Noble metal nanoparticles (including gold nanoparticles) are able to pass through the walls of blood vessels into the neoplastic tissue and accumulate in tumor cells (Minelli et al. 2010; Conde et al. 2012). The efficacy of passive targeting is limited by the fact that some parts of the vascular endothelium have a normal structure and nanomaterial extravasation is restricted (Zhang et al. 2014). This phenomenon is easily observed in the case of brain tumors. Enhanced vascular permeability and retention of nanomaterials are significantly lower in cranial tumors compared with peripheral cancer tissues. Moreover, nanostructures can be used for passive targeting in brain tumors, especially after disruption of the blood-brain barrier (BBB) (Liu and Lu 2012; Gao 2016).

2.4.2 Active Targeting

Targeted therapy is based on the use of active compounds able to modulate the activity of specific target molecules, usually through specific recognition and ligand-receptor interactions (Zhang et al. 2014).

For successful/efficient active targeting, extravasation of nanomaterials into the neoplastic tissue is necessary (Zhang et al. 2014). Compared with other therapeutic systems, nanomedicines are more likely to reach the target organ and to accumulate and deliver therapeutic agents to cancer tissues (Anselmo and Mitragotri 2015, 2016a).

As target molecules can also be expressed on normal cells, where they perform physiological functions, chemotherapy is associated with a certain degree of toxicity (Widakowich et al. 2007). Although the level of acceptable toxicity of chemotherapeutic agents increases with the severity of cancer (Szabo 2006), the risk-benefit ratio has to be considered when choosing the treatment method. One advantage of using functionalized inorganic nanomaterials in cancer therapy is their ability to accumulate preferentially at tumor site, leading to reduced overall toxicity by limiting the damage to normal tissues and consequent side effects.

Vascular Targeting

Solid tumors require access to blood vessels for growing and metastasis. Tumor evolution includes angiogenesis, vasculogenesis (in both normoxic and hypoxic conditions, result of proliferation and migration of endothelial cells), and vasculogenic mimicry (without endothelial cell participation, hypoxic conditions). Vasculogenic mimicry is often associated with high multidrug resistance (MDR) and the ability to generate different cell types and to increase tumor heterogeneity (Kirschmann et al. 2012; Wangeblast et al. 2015; Spiliopoulos et al. 2015; Vallée et al. 2018). As a consequence of fast development of the neoplastic tissue, which requires high amounts of nutrients, tumor vessels are usually leaky and dilated and show abnormal structure (Jain 2005). The vascular endothelial growth factor (VEGF), the main mitogenic factor for endothelial cells, is one of the main factors that promote angiogenesis (being overexpressed in the majority of solid tumors) and is also involved in immunosuppression (inhibits T cell activation, inhibits NF-kB activation in dendritic cells) (Jain 2005; Zitoogel et al. 2006; Knopik-Skrocka et al. 2017). Thus, the inhibition of VEGF in neoplastic tissues would expectedly lead toward “normalized vasculature” (with less altered structure and function) and subsequent tumor weight reduction.

Since the precise control of spatial and temporal distribution of VEGF is essential for maintaining the structure and function of normal vasculature, targeting VEGF at tumor level without altering normal tissues represents one of the most challenging therapeutic approaches. Experimental in vivo data has shown that nanomedicine-based targeting of VEGF and other vascular biomarkers is a very efficient strategy to inhibit tumor growth and to reach micrometastases (Toy et al. 2014).

Some recent studies have shown that some inorganic nanomaterials alone or conjugated with ligands of VEGF receptors (e.g., gold nanoparticles, VEGF-121-conjugated mesoporous silica) have antiangiogenic properties (Mukherjee et al. 2005; Goel et al. 2014). Blocking angiogenesis, however, has cytostatic, but not cytotoxic, effect, the surviving cancer cells being able to develop a more malignant phenotype and contribute to tumor invasion and metastasis. A combined therapy – VEGF inhibitors and cytotoxic agents – is thus required for an effective antitumor action. VEGF inhibitors induce important side effects such as hypertension, arterial thromboembolic events, and wound-healing complications (Laschke et al. 2006; Meadows and Hurwitz 2012; Chen and Hung 2013).

As tumor growth is driven mainly by cancer stem cells, Ambasta et al. proposed twin nanoparticles gold-coated SPIONs functionalized with both VEGF monoclonal antibodies and cancer stem cell markers to be used as anticancer nanomedicines. After reaching the tumor under magnetic field guidance and bounding cancer stem cells only, twin nanoparticles unfold and release VEGF antibodies to block angiogenetic pathways (Ambasta et al. 2011).

Tumor Targeting

Tumor Targeting Based on Specific Ligand: Receptor Interaction

Following extravasation from tumor vessels, functionalized inorganic nanomaterials enter the interstitial fluid and interact with different types of cells present in tumor stroma. The nanomaterial-cell interaction depends on cell surface characteristics (e.g., receptor types and distribution), being driven by the chemical affinity between the used functionalized nanomaterial and certain membrane receptors, highly expressed on tumor cells, able to recognize and specifically bind the functionalization agent.

One of the most important cellular receptors involved in cancer progression and metastasis is epidermal growth factor receptor (EGFR). Its internalization (through clathrin-dependent pathway) is associated with inhibition of apoptosis, cell proliferation, invasiveness, and metastasis, as well as angiogenesis (Rocha-Lima et al. 2007). EGFR overexpression is associated with many types of cancer and is due to the sustained production and release of endogenous EGFR receptors in tumor microenvironment (Sasaki et al. 2013) (Table 2.1).

Table 2.1 Inorganic nanostructures with anticancer effect based on epidermal growth factor receptor (EGFR)-specific targeting

	Inorganic nanostructure	Therapeutic agent	Tumor type	Study type (in vivo/ in vitro)	Bibliographic source
1	Carbon nanodiamonds	Paclitaxel	Breast cancer	In vitro	Zhang et al. (2011b)
2	Carbon nanovectors	Cetuximab Paclitaxel	Squamous carcinoma osteosarcoma	In vitro	Berlin et al. (2011)
3	Cyclodextrin-covered gold nanoparticles	B-Lapachone	Breast adenocarcinoma Lung carcinoma	In vitro	Park et al. (2009)
4	Plasmonic gold nanoparticles	Photothermal therapy	Oral squamous carcinoma	In vitro	El-Sayed et al. (2006)
5	Hollow gold nanoshells	Photothermal ablation	Squamous carcinoma	In vitro, in vivo (biodistribution)	Melancon et al. (2008)
6	Gold nanoparticles	Cetuximab	Lung cancer	In vitro, in vivo	Qian et al. (2014)
7	Silica nanoparticles	Cetuximab	Lung cancer	In vitro	Wang et al. (2016)
8	Iron oxide magnetic nanoparticles	Alternating magnetic field	Breast cancer	In vitro	Creixell et al. (2011)
9	Plasmonic magnetic nanoparticles	Magnetic field	Non-small cell lung cancer	In vitro	Yokoyama et al. (2011)
10	Plasmonic magnetic nanoparticles	Magnetic field	Lung cancer	In vitro, in vivo	Kuroda et al. (2014)

In vivo studies using glioblastoma mouse model have shown that administration of gold nanoparticles coated with peptides against multiple receptors (e.g., EGFR and transferrin receptors) resulted in increased specificity and decreased time of maximal accumulation in cells overexpressing both receptors (Dixit et al. 2015). Blocking transferrin receptors leads to decreased iron influx in cancer cells. As iron contributes to the generation of hydroxyl radicals (highly oxidative species able to induce DNA damage and subsequently malignant transformation) by the Fenton reaction, iron depletion could inhibit cancer growth (McCarty et al. 2010; Jiang et al. 2010).

VEGF release is promoted by matrix metalloproteinase-2 (MMP-2) (Kessenbrock and Werb 2010), an endopeptidase whose overexpression on the surface of invasive cancer cells is responsible for degradation of extracellular matrix, migration of tumor cells, invasion, and metastasis (Gialeli et al. 2011). MMP-2 also contributes to angiogenesis and tumor-associated inflammation (Kessenbrock and Werb 2010). Silver/alisertib nanocomposites conjugated with a chlorotoxin which specifically binds to MMP-2 reduced tumor size in glioblastoma-bearing mice (Locatelli et al. 2014).

Other molecules overexpressed on the membrane of tumor cells were specifically targeted using nanoconstructs: single-walled carbon nanotubes (SWNTs) for CD20 antigen overexpressed on human Burkitt lymphoma cells (McDevitt et al. 2007), thiamine-coated gadolinium nanoparticles for binding thiamine transporters in breast cancer cells (Oyewumi et al. 2003), and functionalized gold nanoparticles for targeting protein tyrosine kinase 7 (PTK7) in T cell acute lymphoblastic leukemia (Luo et al. 2011). Unfortunately, specific binding to cancer cells is not necessarily associated with metabolic changes resulting in cancer cell death. Additional targeting strategies are needed to act after nanomedicine internalization in the cell, for example, by inhibiting an altered signaling pathway or inducing apoptosis through physical factors (e.g., hyperthermia).

Intracellular Targeting

Following internalization in tumor cells, the drug is released by either external activating stimuli (magnetic field, light, temperature) or intrinsic physicochemical stimuli at the target site (pH, enzyme, redox, etc.) (Zhang et al. 2014).

a) *Altered signaling pathways*

Some signal transduction pathways are altered in both premalignant and late-stage malignant cells (e.g., overexpression of proinflammatory mediators, VEGF, proteolytic enzymes) (Knopik-Skrocka et al. 2017; Steinman and Mellman 2004). For example, overexpression of cyclooxygenase 2 (COX-2) is common to various premalignant and malignant lesions of epithelial cell origin. COX-2 is involved in cancer development through promoting of Th2 responses, inhibition of T cell toxicity, and sustaining angiogenesis (Zitoogel et al. 2006). Park's group has shown that inhibition of COX-2 expression and activity by resveratrol-capped gold NPs led to enhanced inhibition of breast cancer metastasizing process (Park et al. 2016).

In many cancers, at least one signaling pathway is responsible for neoplastic transformation. The simultaneous modulation of the function of multiple biomolecules acting at different points in the same signaling pathway may be more efficient in treating the disease than blocking the function of a single protein encoded by an oncogene (Weinstein and Joe 2006). Moreover, the molecular mediators and corresponding signaling pathways responsible for self-seeding could be, at least partially, the same in the primary tumor site and metastatic site (Norton and Massagué 2006). This feature creates premises for using inorganic nanomaterial-based medicines that are effective on both primary and secondary tumors.

b) *Multidrug resistance (MDR)*

MDR, the acquired loss of sensitivity of tumor cells to multiple chemotherapeutic agents, is one of the most important factors responsible for failure in cancer treatment. MDR is a consequence of repeated exposure of tumor cells to subtherapeutic doses of anticancer drugs, resulting in reduced retention of chemotherapeutics in the cells (due to overexpression of multidrug efflux pumps) and altered apoptosis (Krishnan and George 2014).

By preferentially accumulating in tumor cells and by delivering higher amounts of anticancer compounds than classical therapies, functionalized inorganic nanomaterials can contribute to the reduction of MDR, thus making tumor cells more susceptible to chemotherapeutic agents.

Nanomaterial-based therapeutic approaches to overcome MDR include the conjugation of nanomaterials with an anticancer drug: (a) an inhibitor of MDR pumps expression and activity, (b) a proapoptotic agent, and (c) microRNA or small interfering RNA aimed at blocking the expression of MDR genes (Chen et al. 2009; Gao et al. 2012; Peetla et al. 2013).

One class of representative conventional therapeutic agents associated with efficacy in killing tumor cells but also with high systemic toxicity and development of multidrug resistance is represented by platinum derivatives.

Despite their efficacy in killing tumor cells, platinum-based anticancer drugs are associated with high systemic toxicity and development of multidrug resistance. However, conjugating platinum-based anticancer drugs with gold nanoparticles and nanorods or iron oxide nanoparticles allows targeted therapy, being able to increase the drug uptake in tumor cells and to reduce multidrug resistance in lung cancers (Ma et al. 2015).

Although numerous studies indicate that the use of nanomaterial-based nanomedicines represents a promising way to reduce the MDR induced by standard antitumor approaches, the possible occurrence of MDR as a consequence of suboptimal doses of such therapeutic nanostructures has not been excluded yet.

c) *Exosome secretion*

Trafficking biological material (key proteins, microRNA) outside cancer cells contributes to cell-cell interaction, tumor microenvironment maturation, invasiveness, and metastasis (Azmi et al. 2013; Roma-Rodrigues et al. 2017). Circulating exosomes contain combinations of molecules (key proteins, mRNA, noncoding

RNAs including microRNAs, DNA) representing the originating cell and reflect tumor stage and specificity, being considered biomarkers of particular neoplastic diseases. Moreover, exosomes secreted by tumor cells can modulate the phenotype and genotype of recipient cells, contributing to pre-metastatic phenotype acquiring and metastasis (van der Vos et al. 2011; Peinado et al. 2012). Secretion of exosomes containing chemotherapeutic drugs is part of the multidrug resistance that tumor cells develop after the onset of specific therapy (Peinado et al. 2012).

Significant amounts of data showed that gold nanoparticles coated with siRNA or antibodies against key proteins can inhibit exosome genesis and secretion, as well as exosome uptake in secondary cells (see Roma-Rodrigues et al. systematic review) (Peinado et al. 2012).

2.4.3 The Use of Nanomaterials in Tumor Surgery

One potential use of nanomaterials in tumor surgery is the vital staining of sentinel lymph nodes (SLNs) that drain the region in which cancer is located. Since SLNs are the structures where first metastases are expected to develop, their surgical removal hinders the metastatic process.

Carbon nanoparticles injected into peritumoral tissue are phagocytosed by macrophages, taken up selectively by lymphatic vessels, and retained into SLNs (Lu et al. 2017).

Carbon nanoparticle-loaded SLNs turn black and facilitate surgeons to harvest them in order to reduce the chance of further metastasis (Wu et al. 2015).

The peritumoral injection of carbon nanoparticles in patients with colorectal carcinoma or advanced gastric cancer was associated with a significantly higher number of harvested SLNs compared with their corresponding controls (Cai et al. 2012; Yan et al. 2014; Li et al. 2016a).

Based on the same therapeutic approach, very recent clinical trials showed encouraging results in breast and cervical tumors (Lu et al. 2017; Wu et al. 2015), lung cancer (He et al. 2010), and papillary thyroid carcinoma (Xu and Gu 2016; Yu et al. 2016).

Based on their broad absorption spectrum, single-walled and multilayer carbon nanotubes could also be used for enhanced photoacoustic identification (PA) of SLNs (including deep tissue imaging) (Pramanik et al. 2009). However, since both single-walled and multilayer carbon nanotubes showed increased toxicity in vitro and in vivo (animal models) (Muller et al. 2005; Wang et al. 2012b; Takanashi et al. 2012; Zhang et al. 2013), the biocompatibility of carbon nanotubes has to be further investigated.

Recent findings (in vivo studies and clinical trials) indicate superparamagnetic iron oxide nanoparticles (SPIONs) as a feasible alternative for identifying SLNs in breast cancer (Finas et al. 2012; Pouw et al. 2015) and prostate carcinoma (Winter et al. 2014). As SPIONs are driven by magnetic field from injection site to lymph nodes, they are capable to move through both lymphatic vessels and lymph-fat tissue (Finas et al. 2012; Pouw et al. 2015; Winter et al. 2014). However, SPION's ability (guided by an external magnetic field) to move at different rates across all types of soft tissue can also lead to accumulation in other structures than lymph nodes. A good expertise of the surgeon is needed for a good intraoperative identification and removal of SLNs.

In all cases, SLN dissection is associated with significant side effects such as lymphedema, seroma, pain, and difficulty in moving the affected part of the body. Under these circumstances, nanomaterial-based lymphatic mapping helps to avoid extensive lymph node surgery by harvesting the metastatic nodules only, ultimately benefiting the patients.

A second potential application of nanomaterials in surgical procedures (including tumor surgery) involves nanoparticle-based medical adhesives used for surgical wound closure (Rose et al. 2014; Meddahi-Pellé et al. 2014). Using an animal experimental model (rats), Leibler et al. showed that an aqueous suspension of iron oxide and silicon dioxide nanoparticles (50 nm) is able to rapidly connect highly vascularized tissues (e.g., liver) as well as to glue medical devices or bioengineered constructs to internal organs (Rose et al. 2014). The potential for clinical applications of these nanoparticle-based adhesives is significant in most cases: cancer surgery is highly invasive and associated with massive bleeding which requires large and complex sutures. By reducing surgery-associated pain and loss of blood, such nanostructured medical adhesives would speed up the recovery in patients after surgical intervention.

2.4.4 *Nanomaterial-Enhanced Radiotherapy*

Both theoretical and in vivo studies showed that gold nanoparticles can successfully act as inorganic sensitizers for kilovoltage radiotherapy, leading to significantly enhanced antitumor effect compared with radiotherapy alone (Smith et al. 2012; Hainfeld et al. 2008; Yao et al. 2016). For example, the 1-year survival rate increased from 20% (control group) to 86% in mice with mammary tumors treated with gold nanoparticles and radiotherapy (Hainfeld et al. 2008). No similar results were obtained so far for TiO_2 nanoparticles (used as sensitizers in photodynamic therapy) (Smith et al. 2012).

The main advantage of using inorganic nanomaterials to enhance the effect of radiotherapy is that the radiations can be reached more quickly in cancer tissues (due to preferential accumulation of nanomaterials in the neoplastic region) compared with normal tissues. This aspect is very important given that radiotherapy alone is not tumor specific.

2.4.5 Iron Replacement Therapy

Iron oxide colloids (IOC) (iron dextran, iron sucrose, iron gluconate, and iron carboxymaltose colloids) are useful adjuvants in antitumor therapy, in treating iron-deficient anemia associated with cancer, especially in advanced stages of the disease (Anselmo and Mitragotri 2016b). IOC are more efficient and have lower associated risks compared with free iron (Anselmo and Mitragotri 2016b).

2.4.6 Antitumor Hyperthermia

Hyperthermia is a cancer treatment method in which body tissue is exposed to high temperatures (up to 45 °C). Such temperatures can kill cancer cells while producing minimal damage to normal tissue.

Hyperthermia alters the fluidity and stability of cell membranes and cytoskeletal organization, leads to denaturation of cellular proteins, and hinders the repairing of radiation-induced DNA damage. By increasing the expression level of heat shock proteins which, in combination with tumor-specific proteins, promotes the activation of T cells against tumor cells, hyperthermia increases the immunogenicity of the tumor (Hildebrandt et al. 2002). The thermal dose required to induce hyperthermic cell death varies significantly between different types of cells.

Magnetic Nanoparticles: Heat Dissipation Under Alternating Magnetic Fields

When magnetic nanoparticles are excited by external variable magnetic fields, they dissipate energy in the form of heat into the surrounding environment (Landi 2013; Wildeboer et al. 2014; Rosensweig 2002). A discussion regarding the physical mechanisms of magnetic heat generation goes beyond the purpose of this book chapter.

The parameter that characterizes the heating efficiency is the specific absorption rate (SAR), defined as

$$SAR = c\frac{\Delta T}{\Delta t} \tag{2.24}$$

In Eq. 2.24, c is the specific heat capacity, measured in $\mathrm{JK}^{-1}\,\mathrm{kg}^{-1}$, and ΔT is the temperature rise during the time interval Δt. Thus, the SAR represents the heating power generated per unit mass of magnetic nanomaterial.

The experimental determination of SAR is based on the analysis of the heating curves, *T(t)*, recorded for magnetic fluid samples (magnetic colloids) exposed to alternating magnetic fields. Various discussions on methods for SAR calculation can be found in the literature (Wildeboer et al. 2014).

The efficacy of biocompatible magnetic nanoparticles as heat sources for antitumor hyperthermia was investigated in animal models (Balivada et al. 2010; Hu et al. 2011; Arriortua et al. 2016) and, rarely, in clinical trials (Johannsen et al. 2007a, b). Efficient and well-localized ablation of mice carcinomas (78%–90% with respect to controls) was achieved using hyperthermia induced by commercial Fe_3O_4 nanoparticles coated with PEG, treating tumors being resorbed in 1–2 days (Huang and Hainfeld 2013). The significant success of the used method originated in multiple factors such as intravenous delivery (adequate for loading carcinoma), low systemic toxicity of the therapeutic nanoparticles, good magnetic material localization in the tumor region, and efficient heating (due to material and applied field characteristics) (Huang and Hainfeld 2013).

Superparamagnetic nanoparticles were used in an extended clinical study aiming to assess hyperthermia-related morbidity and quality of life in patients with locally recurrent prostate cancer (biopsy-proven). Ten patients without metastasis were enrolled in a phase I clinical trial (Johannsen et al. 2007a, b). The magnetic fluid was injected into the cancer tissue transperineally, and alternating magnetic fields were applied in order to deliver thermal therapy. Each patient received six 60-min-long treatment sessions at weekly intervals. The procedure was feasible and well tolerated in patients with locally recurrent prostate cancer, hyperthermic to thermoablative temperatures being achieved in the tumor tissue at 25% of the available magnetic field strength.

Plasmonic Photothermal Therapy (PPTT)

Photothermal therapy (PTT) is a type of antitumor hyperthermia in which the heat is generated by conversion of photon energy through surface plasmon resonance (SPR). SPR occurs due to the interaction of conduction electrons of metal nanoparticles with incident light beams, radio-/microwaves, or sound waves. The interaction depends on the size and shape of the metal nanoparticles and on the characteristics (state, composition) of the dispersion medium.

The therapeutic applications of visible PPTT are limited since visible light cannot penetrate deep into the tissue. Near-infrared (NIR) light, however, is minimally absorbed by hemoglobin and water molecules, and it is preferred for in vivo studies and therapy (Huang and El-Sayed 2011).

Using a mouse model and gold nanoshells intratumorally injected, Halas et al. showed that breast cancer-xenografted tumors were destroyed after several minutes of NIR laser irradiation. Subsequent studies revealed that more than half of treated mice experienced complete eradication of the tumors with no regrowth after 90 days. Liver- and spleen-accumulated gold nanospheres started to be eliminated out of the body after 6 months (O'Neal et al. 2004; James et al. 2007).

Li et al. studied the importance of targeting for the efficiency of PPTT with gold nanocages (Lu et al. 2009). The used targeting ligand was a synthetic analog of α-melanocyte-stimulating hormone (MSH) that targets the melanocortin type 1 receptor overexpressed in melanoma tumors xenografted in mice. Results indicated significantly increased tumor affinity and reduced metabolic activity (associated with necrotic response by histologic examination) after targeted PPTT compared to the non-targeted case.

The obtained results suggest that NIR-absorbing plasmonic nanoparticles are good candidates for antitumor PPTT.

The heat generated during PPTT can also be used to optically induce the release of drugs transported via plasmonic nanoshells (nanostructures composed of a dielectric core coated with a metal shell) embedded in thermally responsive polymers that form hydrogels. The hydrogels store the drug solution and expel it when heated by PPTT (Sershen et al. 2001).

Irrespective of the heat generation mechanism, hyperthermia represents an adjuvant cancer therapy which enhances the efficiency of conventional methods by influencing the blood flow, oxygen, and nutrient supply and the immune response in tumor stroma. Heat effects alone are not sufficient to replace conventional cancer treatment strategies.

2.4.7 Photodynamic Therapy (PDT)

Photodynamic therapy (PDT) is defined by the American Cancer Society as "a treatment that uses special drugs, called *photosensitizing agents,* along with light to kill cancer cells" (https://www.cancer.org/treatment/treatments-and-side-effects/treatment-types/photodynamic-therapy.html). Light-activated chemotherapeutic agent allows PDT to be minimally invasive and precisely targeted to the tumor tissue. Clinical applications of PDT are limited though, because the light is not able to reach deep tissues in the body to activate the photosensitizers (You et al. 2016). Nanoparticles may act as "passive" PDT agents (carriers of photosensitive drugs) or "active" PDT agents (when nanoparticles generate ROS on their surface). While gold and silica nanoparticles have been used as passive carriers of photosensitizers (Smith et al. 2012; Chatterjee et al. 2008), TiO_2 gives the most representative example of "active" PDT nanoparticles, based on its photocatalytic properties (Smith et al. 2012; Chatterjee et al. 2008).

Photocatalysis refers to the ability of some solid semiconductor materials to initiate and sustain certain surface chemical reactions when acted upon by light at different wavelengths. The semiconductor is assumed to act only as a reaction substrate and charge carrier source while remaining chemically unaltered during the catalytic process.

General Description of Photocatalysis

When a semiconductor particle is immersed into an aqueous solution, ions or molecules in that solution may be adsorbed or chemically bounded on the surface of the particle. As an example, titanium dioxide TiO_2 has the tendency to become hydroxylated due to the binding of hydroxyl groups on its surface (Carp et al. 2004).

Electrostatic forces may also play a significant role, leading to the accumulation of undissolved ions at the semiconductor-solution interface. These forces appear due to the presence of charge carriers – electrons and holes – in the near-surface region of the semiconductor particle. Carriers are generated in the bulk, or near the surface of the particle, when this is exposed to light of sufficient energy to induce relevant electronic transitions within the semiconductor. On the surface of the semiconductor, these charge carriers can produce oxidation or reduction of adsorbed molecules, leading to specific chemical reactions. Photocatalysis is thus a complex process involving semiconductor physics as well as interface and chemical phenomena. Although the literature comprises a large number of studies concerning different photogenerated species like electrons and holes (Dung et al. 1982; Rothenberger et al. 1985; Kamat 1985), superoxide (Ishibashi et al. 1998), singlet oxygen (Hirakawa and Hirano 2006; Nosaka et al. 2004), hydrogen peroxide (Kubo and Tatsuma 2004), and hydroxyl radicals (Murakami et al. 2006), the discussion is still far from being closed (Eberl 2008).

In case of systems composed of different types of molecules, the overall absorbance of the system is the sum of absorbances corresponding to each type of molecule.

The ability of TiO_2 nanoparticles to induce ROS-mediated toxicity under normal conditions (Fujiwara et al. 2015; Ramires et al. 2001; Peters et al. 2004; Gurr et al. 2005; Dubey et al. 2015; Popescu et al. 2016; Long et al. 2006) or when they are photoactivated (You et al. 2016; Zhang and Sun 2004; Rozhkova et al. 2009; Moosavi et al. 2016) was considered as an alternative to conventional ROS-generating chemotherapeutic agents. One of the main advantages of using TiO_2 NPs as therapeutic agents is the high stability of TiO_2 to degradation by ROS (You et al. 2016).

Rozhkova et al. used undoped 5 nm TiO_2 nanoparticles conjugated with IL13α2R-targeting antibody (anti-human-IL13α2R) to target and destroy malignant glioma (glioblastoma multiforme (GBM)) brain tumor cells. Results indicated that the used nanoconjugates bind exclusively to GBM cells and, under exposure to visible light, initiate the production of ROS, damaging the cell membrane and inducing apoptosis of the cancer cells (Rozhkova et al. 2009).

Efficient PDT was achieved using nitrogen-doped titanium dioxide (N-TiO_2) nanoparticles activated by visible light, which induced in a controlled manner ROS production and subsequent autophagy in leukemia K562 cells and normal peripheral lymphocytes. The observed effect was dependent on nanoparticle concentration and light doses, thus allowing to prime the autophagy (needed for apoptotic cell death) via controlled levels of ROS production (Moosavi et al. 2016). Xie et al. used nitrogen-doped TiO_2 nanoparticles conjugated with folic acid (N-TiO_2-FA) and tested the efficiency of targeting and photodynamic effect on human nasopharyngeal carcinoma (KB) (overexpression of folate receptors (FR)) and human pulmonary adenocarcinoma (A549) (used as FR-negative) cells. The results showed that KB cells had twofold higher uptake efficiency compared to A549 and a significantly higher photokilling effect under visible light irradiation (Xie et al. 2016).

The photodynamic effect of TiO_2-based nanomedicines was also investigated in vivo. For instance, Lucky et al. performed a lengthy and complex study regarding the use of near-infrared (NIR) excitable upconversion TiO_2-based nanoparticle as PDT agents for targeted treatment of head and neck cancers. The used nanostructures were anti-EGFR-PEG-TiO_2 conjugates that targeted the epithelial growth factor receptor (EGFR). Subacute and long-term toxicity was assessed after systemic delivery of a 50 mg/kg dose of PDT nanomedicine, based on blood biochemical, hematological, or histopathological changes. Results showed no major toxic effect induced by the tested nanomedicine. Moreover, significant delays in tumor growth and enhanced survival rates were observed in mice treated with the TiO_2-based nanomedicine compared to conventional chlorin-e6 (Ce6) PDT (Lucky et al. 2016).

2.5 Discussion

One important cause for the huge mortality of cancer is its late detection. Cancer develops as an insidious disease and clinical symptoms, which send the patient to the doctor, appear in already advenced stages. Cancer prevention and early therapeutic intervention are of primary importance.

Even if it is conceivable, inorganic nanoparticles (functionalized or not) are not used in cancer prevention yet. In turn, they are widely used as contrast agents for imaging (e.g., MRI) as well as for analytical detection of tumor-associated biomarkers (Krishnan and George 2014; Oyarzun-Ampuero et al. 2015).

A significant number of studies are dedicated to finding an anticancer vaccine which, similar to classical vaccines, simulates an infection and stimulates the immune system to fight against the “pathogen.” The efficacy is limited though. Unlike classical vaccines which have a preventive role, anticancer vaccine should work after the onset of the disease, when the interactions between the immune system and the tumor cells are already changing.

Since the antigen expression of premalignant and early stage cancer cells is often similar to that of normal cells, growth of cancer is not accompanied by strong “danger signals” and proinflammatory signals, and the immune system does not initiate an effective antitumor response (De Vries and Figdor 2016).

As tumor microenvironment is usually hypoxic, infiltrating immune cells are inhibited and become unable to initiate and sustain a strong immune response anymore, even if cancer cells present antigens that normal cells don’t usually express. Moreover, a wide variety of chemokines secreted by tumor cells contributes to induce tolerance in immune cells and immunosuppression (De Vries and Figdor 2016; Prado-García and Sánchez-García 2017; Hagerling et al. 2015).

Despite the fact that neoplastic transformation and tumor growth represent consequences of combined multiple genetic lesions, in some cases a dominant oncogene seems to be sufficient for cancer development. The inhibition of this specific oncogene could lead to the inhibition of malignant phenotype (Norton and Massagué 2006). Targeting this “oncogene addiction” is a challenge for anticancer gene-targeted therapy. Even if some inorganic nanomaterials (e.g., gold nanoparticles) are able to efficiently deliver nucleic acids to tumor cells (Conde et al. 2012; Kouri et al. 2015; Frosina 2016; Mendez et al. 2017), no inorganic nanomaterial-based gene-targeting agent was introduced so far in anticancer clinical care.

Nanomaterials used in cancer therapy must not induce, promote, or maintain tumorigenesis and/or metastasis. If during premalignant stages immune system contributes to the recognition and destruction of transformed cells, in more advanced stages, immune processes are partially reprogrammed, and inflammation switches from friend to foe and promotes tumor development and metastasis by creating a mutagenic microenvironment able to accelerate cell transformation or to induce new mutagenic events (Hagerling et al. 2015; Grivennikov et al. 2010; Candeias and Gailp 2016). In advanced cancer patients, systemic inflammation is already installed, and eventual accumulation in non-tumor tissues of nanomaterials known to induce excessive ROS generation and activate inflammatory signaling pathways should be considered as potential disease-promoting factor. Further extensive studies are needed to establish dose ranges and treatment schemes for inorganic nanomaterial-based therapeutic agents.

As moderate oxidative stress (mediated especially through superoxide and hydrogen peroxide signaling) stimulates survival and proliferation of malignant transformed cells (Afanas’ev 2011), it is possible that nanomaterials with low toxicity for the organism to produce insufficient amounts of ROS and, in fact, to promote tumor development. Finding ways to increase the generation of ROS by nanomaterials at the tumor site only or to make cancer cells more susceptible to the proapoptotic action of ROS is of major importance for the therapeutic quality of inorganic nanomaterials. On the other hand, when designing and testing ROS generating nanomaterials functionalized with antitumor agents, one should consider the stability of the functionalizing agent against the action of ROS directly released by nanomaterial.

Moreover, since the same drug may act in different ways due to variation in gene expression for the corresponding drug-metabolizing enzymes (Karlow 2006), the therapeutic doses need to be permanently correlated with patient’s metabolic response.

The assessment of anticancer effectiveness of nanomaterial-based nanomedicines against their adverse effects requires data regarding implications of long-term exposure to the used inorganic nanomaterials. It is already known that metal oxide nanoparticles (e.g., titania nanoparticles) and carbon nanoparticles can lead to inflammatory responses (Dubey et al. 2015; Long et al. 2006; Niwa et al. 2008). The side effects of silica nanoparticles are related to cellular immunity (splenocyte proliferation associated with phenotypic alteration of spleen-derived lymphocytes, increase in NK and T lymphocyte distribution, decrease of B cell distribution) (Park and Park 2008). Nanoparticles can also induce epigenetic effects. Li et al. (2016b) demonstrated that both single-walled and multi-walled carbon nanotubes significantly increase DNA methylation in A549 cell line (human lung epithelial cells) (Li et al. 2016b). The possibility of MDR development as a result of long-term exposure to nanomedicines containing inorganic nanoparticles should also be taken into consideration in future studies.

Since there are no standard in vitro methods to evaluate the biocompatibility and antitumor effects of inorganic nanomaterials and considering the multitude of nanomaterial types and properties obtained by different synthesis methods, it is difficult to compare results obtained by different research groups using different materials, cell lines, and bioassays.

The currently available body of scientific data was mainly obtained based on in vivo studies, using animal species with different genetic background and metabolic pathways as well as different amplitude of response compared with humans. For example, the metabolic processes in mice are faster than in humans, and higher concentrations of therapeutic compounds can be used in mice compared with humans. Moreover, differences between human and murine immune systems significantly influence both the onset and the progression of tumors (Zitoogel et al. 2006; Mestas and Hughes 2004), and animal studies have a limited predictive value regarding cancer evolution in humans. Good evaluation of previous published data and rigorous methodological flow in animal studies are key players in nanomedicine research translation toward clinical trials (van der Worp et al. 2010).

Various formulations of nanomedicines can be designed based on the same type of inorganic nanomaterial, by engineering its physicochemical properties and using different functionalization agents. For already approved nanomedicines containing inorganic nanomaterials, additional studies are needed to identify potential applications of inorganic nanomaterials in treating additional cancer types or for new combinations with other therapeutic agents.

Numerous studies have revealed the valuable potential of inorganic nanomaterials for applications in cancer therapeutics. Based on their specific physicochemical properties, nanomaterials offer new antitumor action principles associated with innovative physical therapeutic methods such as magnetic hyperthermia, plasmon photothermal therapy, and photodynamic therapy. By surface functionalization with therapeutic molecules, nanomaterials can exert targeted antitumor action with higher efficiency, lower adverse effects, and diminished multidrug resistance in comparison with standard therapeutic approaches.

At present, nanomedicines based on inorganic nanomaterials can only be conceived as adjuvant therapeutic strategies against cancer. Further research endeavors are required in order to establish weather inorganic nanomaterials can lead to standalone treatment methods against neoplastic diseases.

Acknowledgments Author Traian Popescu acknowledges funding from Romanian National Authority for Scientific Research, under Core Project PN16480101, and from Romanian Ministry of Research and Innovation, CCCDI – UEFISCDI, under national grant PN-III-P1-1.2-PCCDI-2017-0062/contract no. 58/component project no.1. Author Andreea-Roxana Lupu acknowledges support under PN-II-PT-PCCA-2013-4-1386 (NANOPATCH) and PN-III-P1-1.2-PCCDI-2017-0062/contract no. 58/component project no.1. Andreea-Roxana Lupu and Marko Stojanović were also supported by South East Europe Cooperation, University of Hamburg.

References

Afanas'ev I (2011) Reactive oxygen species signaling in cancer comparison with aging. Aging Dis 2(1):219–230, PMID 22396874

Aggarwal P, Hall JB, McLeland CB, Dobrovolskaia MA, McNeil SE (2009) Nanoparticle interaction with plasma proteins as it relates to particle biodistribution, biocompatibility and therapeutic efficacy. Adv Drug Deliv Rev 61:428–437. https://doi.org/10.1016/j.addr.2009.03.009

Ambasta RC, Sharma A, Kumar P (2011) Nanoparticle mediated targeting of VEGFR and cancer stem cells for cancer therapy. Vasc Cell 3, PMC3226586

Anselmo AC, Mitragotri S (2015) A review of clinical translation of inorganic nanoparticles. AAPS J 17(5):1041–1054. https://doi.org/10.1208/s12248-015-9780-2

Anselmo AC, Mitragotri S (2016a) A chemical engineering perspective of nanoparticle-based targeted drug delivery: a unit process approach. AICHE J 62(4):966–974. https://doi.org/10.1002/aic.15189

Anselmo AC, Mitragotri S (2016b) Nanoparticles in the clinic. Bioeng Transl Med 1:10–29. https://doi.org/10.1002/btm2.10003

Anshup A, Venkataraman JS, Subramaniam C, Kumar RR, Priya S, Kumar TR, Omkumar RV, John A, Pradeep T (2005) Growth of gold nanoparticles in human cells. Langmuir 21 (25):11562–11567. https://doi.org/10.1021/la0519249

Arriortua OK, Garaio E, Herrero de la Parte B, et al (2016) Antitumor magnetic hyperthermia induced by RGD-functionalized Fe_3O_4 nanoparticles, in an experimental model of colorectal liver metastases. Sidorenko AS (ed) Beilstein J Nanotechnol 7:1532–1542. https://doi.org/10.3762/bjnano.7.147

Azmi AS, Bao B, Sarkar FH (2013) Exosomes in cancer development, metastasis and drug resistance: a comprehensive review. Cancer Metastasis Rev 32(0). https://doi.org/10.1007/s10555-013-9441-9

Balivada S, Rachakatla RS, Wang H et al (2010) A/C magnetic hyperthermia of melanoma mediated by iron(0)/iron oxide core/shell magnetic nanoparticles: a mouse study. BMC Cancer 10:119. https://doi.org/10.1186/1471-2407-10-119

Berlin JM, Pham TT, Sano D, Mohamedali KA, Marcano DC, Myers JN, Touri JM (2011) Non-covalent functionalization of carbon Nanovectors with an antibody enables targeted drug delivery. ACS Nano 5(8):6643–6650. https://doi.org/10.1021/nn2021293

Berne BJ, Pecora R (1976) Dynamic light scattering with applications to chemistry, biology, and physics. Wiley-Interscience, New York

Bulte JWM, Kraitchman DL (2004) Monitoring cell therapy using iron oxide MR contrast agents. Curr Pharm Biotechnol 5(6):567–584, PMID:15579045

Bussard KM, Mutkus L, Stumpf K, Gomez-Manzano C, Marini FC (2016) Tumor-associated stromal cells as key contributors to te tumor microenvironment. Breast Cancer Res 18:84. https://doi.org/10.1186/s13058-016-0740-2

Cai HK, He HF, Tian W, Zhou MQ, Hu Y, Deng YC (2012) Colorectal cancer lymph node staining by activated carbon nanoparticles suspension in vivo or methylene blue in vitro. World J Gastroenterol 18(42):6148–6154. https://doi.org/10.3748/wjg.v18.i42.6148

Candeias SM, Gailp US (2016) The immune system in cancer prevention, development, and therapy. Anti-Cancer Agents Med Chem 16(1):101–107, PMID: 26299661

Caracciolo G, Farokhzad OC, Mahmoudi M (2017) Biological identity of nanoparticles in vivo: clinical implications of the protein Corona. Trends Biotechnol 35(3):257–264. https://doi.org/10.1016/j.tibtech.2016.08.011. Epub 2016 Sep 20

Carp O, Huisman CL, Reller A (2004) Photoinduced reactivity of titanium dioxide. Prog Solid State Chem 32:33–177. https://doi.org/10.1016/j.progsolidstchem.2004.08.001

Cedervall T, Lynch I, Lindman S, Berggard T, Thulin E, Nilsson H, Dawson KA, Linse S (2007) Understanding the nanoparticle-protein corona using methods to quantify exchange rates and affinities of proteins for nanoparticles. Proc Natl Acad Sci USA 104:2050–2055. https://doi.org/10.1073/pnas.0608582104

Chatterjee DK, Fong LS, Zhang Y (2008) Nanoparticles in photodynamic therapy: an emerging paradigm. Adv Drug Deliv Rev 60(15):1627–1637. https://doi.org/10.1016/j.addr.2008.08.003

Chen C-T, Hung M-C (2013) Beyond anti-VEGF: dual-targeting antiangiogenic and antiproliferative therapy. Am J Transl Res 5(4):393–403, PMCID: PMC3665913

Chen AM, Zhang M, Wei D, Stueber D, Taratula O, Minko T, He H (2009) Co-delivery of doxorubicin and Bcl-2 siRNA by mesoporous silica nanoparticles enhances the efficacy of chemotherapy in multidrug-resistant cancer cells. Small 5:2673–2677. https://doi.org/10.1002/smll.200900621

Commission E (2011) Commission recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU), vol L275/38

Conde J, Doria G, Baptista P (2012) Noble metal nanoparticles applications in Cancer. J Drug Deliv, Article ID 751075, 12 pages. https://doi.org/10.1155/2012/751075

Creixell M, Bohórquez AC, Torres-Lugo M, Rinaldi C (2011) EGFR-targeted magnetic nanoparticle heaters kill cancer cells without a perceptible temperature rise. ACS Nano *5*(9):7124–7129. https://doi.org/10.1021/nn201822b

De Vries J, Figdor C (2016) Cancer vaccine triggers antiviral-type defences. Nature 534:329–331. https://doi.org/10.1038/nature18443

Dixit S, Miller K, Zhu Y, Mc Kinnon E, Novak T, Kenney ME, Broome AM (2015) Dual receptor-targeted theranostic nanoparticles for localized delivery and activation of PDT drug in glioblastomas. Mol Pharm. https://doi.org/10.1021/acs.molpharmaceut.5b00216

Doherty GJ, McMahon HT (2009) Mechanisms of endocytosis. Annu Rev Biochem 78:857–902. https://doi.org/10.1146/annurev.biochem.78.081307.110540

Donaldson K, Poland CA, Murphy FA, MacFarlane M, Chermova T, Schinwald A (2013) Pulmonary toxicity of carbon nanotubes and asbestos – similarities and differences. Adv Drug Deliv Rev 65:2078–2086. https://doi.org/10.1016/j.addr.2013.07.014

Dubey A, Goswami M, Yaday K, Chaudhary D (2015) Oxidative stress and nano-toxicity induced by TiO_2 and ZnO on WAG cell line. PLoS One 10(5):e0127493. https://doi.org/10.1371/journal.pone.0127493

Dung D, Ramsden J, Graetzel M (1982) Dynamics of interfacial electron transfer processes in colloidal semiconductor systems. J Am Chem Soc 104:2977–2985. https://doi.org/10.1021/ja00375a006

Eberl J (2008) Visible light photo-oxidations in the presence of bismuth oxides. PhD thesis, Friedrich-Alexander-Universitat, Erlangen-Nurnberg. http://opus4.kobv.de/opus4-fau/files/694/JoachimEberlDissertation.pdf

Eleonore Fröhlich E (2012) The role of surface charge in cellular uptake and cytotoxicity of medical nanoparticles. Int J Nanomedicine 7:5577–5591. https://doi.org/10.2147/IJN.S36111

El-Sayed IH, Huang X, El-Sayed MA (2006) Selective laser photo-thermal therapy of epithelial carcinoma using anti-EGFR antibody conjugated gold nanoparticles. Cancer Lett 239(1):129–135. https://doi.org/10.1016/j.canlet.2005.07.035

Esipova TV, Ye X, Collins JE, Sakadžić S, Mandeville ET, Murray CB, Vinogradov SA (2012) Dendritic upconverting nanoparticles enable in vivo multiphoton microscopy with low-power continuous wave sources. Proc Natl Acad Sci U S A 109(51):20826–20831. https://doi.org/10.1073/pnas.1213291110

Farokhzad OC, Langer R (2009) Impact of nanotechnology on drug delivery. ACS Nano 3:16–20. https://doi.org/10.1021/nn900002m

Finas D, Baumann K, Heinrich K, Ruhland B, Sydow L, Gräfe K, Sattel T, Lüdtke-Buzug K, Buzug T (2012) Distribution of superparamagnetic nanoparticles in lymphatic tissue for sentinel lymph node detection in breast cancer by magnetic particle imaging. In: Buzug TM, Borgert J (eds) Magnetic particle imaging, SPPHY 140. Springer-Verlag, Berlin/Heidelberg, pp 187–191

Fröhlich E, Roblegg E (2012) Models for oral uptake of nanoparticles in consumer products. Toxicology 291(1–3):10–17. https://doi.org/10.1016/j.tox.2011.11.004

Frosina G (2016) Nanoparticle mediated drug delivery to high grade gliomas. Nanomed Nanotechnol Biol Med 12:1083–1093. https://doi.org/10.1016/j.nano.2015.12.375

Fujiwara R, Luo Y, Sasaki T, Fujii K, Ohmori H, Kuniyasu H (2015) Cancer therapeutic effect of titanium dioxide nanoparticles are associated with oxidative stress and cytokine induction. Pathobiology 82:243–251. https://doi.org/10.1159/000439404

Gao H (2016) Progress and perspectives on targeting nanoparticles for brain drug delivery. Acta Pharm Sin B 6(4):268–286. https://doi.org/10.1016/j.apsb.2016.05.013

Gao J, Feng SS, Guo Y (2012) Nanomedicine against multidrug resistance in cancer treatment. Nanomedicine (Lond) 7:465–468. https://doi.org/10.2217/nnm.12.11

Geiser M, Rothen-Rutishauser B, Kapp N, Schürch S, Kreyling W, Schulz H, Semmler M, Im Hof V, Heyder J, Gehr P (2005) Ultrafine particles cross cellular membranes by nonphagocytic mechanisms in lungs and in cultured cells. Environ Health Perspect 113(11):1555–1560. https://doi.org/10.1289/ehp.8006

Gerloff K, Landesmann B, Worth A, Munn S, Palosaari T, Whelan M (2017) The adverse outcome pathway approach in nanotoxicology. Comp Toxicol 1:3–11. https://doi.org/10.1016/j.comtox.2016.07.001

Gessner A, Waicz R, Lieske A, Paulke BR, Mader K, Muller RH (2000) Nanoparticles with decreasing surface hydrophobicities: influence on plasma protein adsorption. Int J Pharm 196:245–249. https://doi.org/10.1016/S0378-5173(99)00432-9

Gialeli C, Theocharis AD, Karamanos NK (2011) Roles of matrix metalloproteinases in cancer progression and their pharmacological targeting. FEBS J 278:16–27. https://doi.org/10.1111/j.1742-4658.2010.07919.x

Goel S, Chen F, Hong H, Valdovinos HF, Hernandez R, Shi S, Barnhart TE, Cai W (2014) VEGF121-Conjugated mesoporous silica nanoparticle: a tumor targeted drug delivery system. ACS Appl Mater Interfaces 6:21677–21685. https://doi.org/10.1021/am506849p

Grivennikov SI, Greten FR, Karin M (2010) Immunity, inflammation and cancer. Cell 140 (6):883–899. https://doi.org/10.1016/j.cell.2010.01.025

Groves E, Dart AE, Covarelli V, Caron E (2008) Molecular mechanisms of phagocytic uptake in mammalian cells. Cell Mol Life Sci 65:1957–1976. https://doi.org/10.1007/s00018-008-7578-4

Gubin SP (ed) (2009) Magnetic nanoparticles. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. https://doi.org/10.1002/9783527627561

Gurr JR, Wang AS, Chen CH, Jan KY (2005) Ultrafine titanium dioxide particles in the absence of photoactivation can induce oxidative damage to human bronchial epithelial cells. Toxicology 213(1–2):66–73. https://doi.org/10.1016/j.tox.2005.05.007

Hagerling C, Casbon A-J, Werb Z (2015) Balancing the innate immune system in tumor development. Trends Cell Biol 25(4):214–220. https://doi.org/10.1016/j.tcb.2014.11.001

Hainfeld JF, Dilmanian EA, Slatkin DN, Smilowitz HM (2008) Radiotherapy enhancement with gold nanoparticles. J Pharm Pharmacol 60(8):977–985. https://doi.org/10.1211/jpp.60.8.0005

Haltiwanger S (2014) Chapter 5. Why electroporation is a useful technique for cancer treatments? In: Sundarajan R (ed) Electroporation-based therapies for cancer: from basics to clinical applications. Elsevier & Woodhead Publishing, Amsterdam, pp 103–118, DOI: 978-907568-15-2 (print)

He J, Li S, Shao W, Wang D, Chen M, Yin W, Wang W, Gu Y, Zhong B (2010) Activated carbon nanoparticles or methylene blue as tracer during video-assisted thoracic surgery for lung cancer can help pathologist find the detected lymph nodes. J Surg Oncol 102(6):676–682. https://doi.org/10.1002/jso.21684

Hildebrandt B, Wust P, Ahlers O, Dieing A, Sreenivasa G, Kerner T, Felix R, Riess H (2002) The cellular and molecular basis of hyperthermia. Crit Rev Oncol Hematol 43:33–56, PMID:12098606

Hirakawa K, Hirano T (2006) Singlet oxygen generation photocatalyzed by TiO_2 particles and its contribution to biomolecule damage. Chem Lett 35:832. https://doi.org/10.1246/cl.2006.832

https://www.cancer.org/treatment/treatments-and-side-effects/treatment-types/photodynamic-therapy.html. Accessed 31 Jan 2017

Hu R, Ma S, Li H et al (2011) Effect of magnetic fluid hyperthermia on lung cancer nodules in a murine model. Oncol Lett 2(6):1161–1164. https://doi.org/10.3892/ol.2011.379

Huang X, El-Sayed MA (2011) Plasmonic photo-thermal therapy (PPTT). Alex J Med 47:1–9. https://doi.org/10.1016/j.ajme.2011.01.001

Huang HS, Hainfeld JF (2013) Intravenous magnetic nanoparticle cancer hyperthermia. Int J Nanomed 8:2521–2532. Published online 2013 Jul 17. https://doi.org/10.2147/IJN.S43770

Ishibashi KI, Nosaka Y, Hashimoto K, Fujishima A (1998) Time-dependent behavior of active oxygen species formed on photoirradiated TiO2 films in air. J Phys Chem B 102:2117–2120. https://doi.org/10.1021/jp973401i

Jain RK (2005) Normalization of tumor vasculature: an emerging concept in angiogenic therapy. Science 307:58–62. https://doi.org/10.1126/science.1104819

James WD, Hirsch LR, West JL, O'Neal PD, Payne JD (2007) Application of INAA to the build-up and clearance of gold nanoshells in clinical studies in mice. J Radioanal Nucl Chem 271:455

Jiang XP, Elliot RL, Head JF (2010) Manipulation of iron transporter genes results in the suppression of human and mouse mammary adenocarcinomas. Anticancer Res 30:759–765, PMID 20392994

Johannsen M, Gneveckow U, Thiesen B, Taymoorian K, Cho CH, Waldöfner N, Scholz R, Jordan A, Loening SA, Wust P (2007a) Thermotherapy of prostate cancer using magnetic nanoparticles: feasibility, imaging, and three-dimensional temperature distribution. Eur Urol 52(6):1653–1661. https://doi.org/10.1016/j.eururo.2006.11.023

Johannsen M, Gneveckow U, Taymoorian K, Thiesen B, Waldöfner N, Scholz R, Jung K, Jordan A, Wust P, Loening SA (2007b) Morbidity and quality of life during thermotherapy using magnetic nanoparticles in locally recurrent prostate cancer: results of a prospective phase I trial. Int J Hyperth 23(3):315–323.B

Kamat PV (1985) Photoelectrochemistry in particulate systems. 3. Phototransformations in the colloidal titania-thiocyanate system. Langmuir 1:608–611. https://doi.org/10.1021/la00065a017

Karlow W (2006) Pharmacogenetics and pharmacogenomics : origin, status and the hope for personalized medicine. Pharmacogenomics J 6:162–165. https://doi.org/10.1038/sj.tpj.6500361

Kessenbrock PV, Werb Z (2010) Matrix metalloproteinases: regulators of the tumor microenvironment. Cell 141(1):52–67. https://doi.org/10.1016/j.cell.2010.03.015

Khan S, Rizvi SM, Ahmad V, Baig MH, Kamal MA, Ahmad S, Rai M, Zafar Iqbal AN, Mushtaq G, Khan MS (2015) Magnetic nanoparticles: properties, synthesis and biomedical applications. Curr Drug Metab 16(8):685–704, PMID: 26264204

Kirschmann DA, Seftor EA, Hardy KM, Seftor REB, Hendrix MJC (2012) Molecular pathways: vasculogenic mimicry in tumor cells; diagnostic and therapeutic implications. Clin Cancer Res 18(10):2726–2732. https://doi.org/10.1158/1078-0432.CCR-11-3237

Knopik-Skrocka A, Kręplewska P, Jarmołowska-Jurczyszyn D (2017) Tumor blood vessels and vasculogenic mimicry – current knowledge and searching for new cellular/molecular targets of anti-angiogenic therapy. Adv Cell Biol 5(1):50–71. Retrieved 22 Jan 2018, from. https://doi.org/10.1515/acb-2017-0005

Kojima S, Negishi Y, Tsukimoto M, Takenouchi T, Kitani H, Takeda K (2014) Purinergic signaling via P2X7 receptor mediates IL-1β production in Kupffer cells exposed to silica nanoparticle. Toxicology 321C:13–20. https://doi.org/10.1016/j.tox.2014.03.008

Kouri FM, Hurley LA, Daniel WL, Day ES, Hua Y, Hao L, Peng C-Y, Merkel TJ, Queisser MA, Ritner C, Zhang H, James CD, Sznajder JI, Chin L, Giljohann DA, Kessler JA, Peter ME, Mirkin CA, Stegh AH (2015) miR-182 integrates apoptosis, growth, and differentiation programs in glioblastoma. Genes Dev 29(7):732–745. https://doi.org/10.1101/gad.257394.114

Krishnan SR, George SK (2014) Nanotherapeutics in cancer prevention, diagnosis and treatment, pharmacology and therapeutics In: Dr Gowder S (ed) InTech. https://doi.org/10.5772/58419

Kubo W, Tatsuma T (2004) Detection of H_2O_2 released from TiO_2 photocatalyst to air. Anal Sci 20:591–595, PMID: 15116953

Kuhn DA, Vanhecke D, Michen B, Blank F, Gehr P, Petri-Fink A, Rothen-Rutishauser B (2014) Different endocytotic uptake mechanisms for nanoparticles in epithelial cells and macrophages. Beilstein J Nanotechnol 5:1625–1636. https://doi.org/10.3762/bjnano.5.174

Kuroda S, Tam J, Roth JA, Sokolov K, Ramesh R (2014) EGFR-targeted plasmonic magnetic nanoparticles suppress lung tumor growth by abrogating G2/M cell-cycle arrest and inducing DNA damage. Int J Nanomed 9:3825–3839. https://doi.org/10.2147/IJN.S65990

Landi GT (2013) Simple models for the heating curve in magnetic hyperthermia experiments. J Magn Magn Mater 326:14–21. https://doi.org/10.1016/j.jmmm.2012.08.034

Larrañeta E, McCrudden MTC, Courtenay AJ, Donnelly RF (2016) Microneedles: a new frontier in nanomedicine delivery. Pharm Res 33:1055–1073. https://doi.org/10.1007/s11095-016-1885-5

Laschke MW, Elitzsch A, Vollmar BB, Vajkoczy P, Menger MD (2006) Combined inhibition of vascular endothelial growth factor (VEGF), fibroblast growth factor and platelet-derived growth factor, but not inhibition of VEGF alone, effectively suppresses angiogenesis and vessel maturation in endometriotic lesions. Hum Reprod 21(1):262–268. https://doi.org/10.1093/humrep/dei308

Li X, Wang L, Fan Y, Feng Q, F-Z C (2012) Biocompatibility and toxicity of nanoparticles and nanotubes. J Nanomater. https://doi.org/10.1155/2012/548389

Li Z, Ao S, Bu Z, Wu A, Wu X, Shan F, Ji X, Zhang Y, Xing Z, Ji J (2016a) Clinical study of harvesting lymph nodes with carbon nanoparticles in advanced gastric cancer: a prospective randomized trial. World J Surg Oncol 24(14):88. https://doi.org/10.1186/s12957-016-0835-3

Li J, Tian M, Cui L, Dwyer J, Fullwood NJ, Shen H, Martin FL (2016b) Low-dose carbon-based nanoparticle-induced effects in A549 lung cells determined by biospectroscopy are associated with increases in genomic methylation. Nat Sci Rep 6, Article number 20207, 11 pages. https://doi.org/10.1038/srep20207

Liu Y, Cao X (2015) The origin and function of tumor associated macrophages. Cell Mol Immunol 12:1–4. https://doi.org/10.1016/0167-5699(92)90008-U

Liu Y, Lu WY (2012) Recent advances in brain tumor targeted nano-drug delivery systems. Expert Opin Drug Deliv 9:671–686. https://doi.org/10.1517/17425247.2012.682726

Locatelli E, Naddaka M, Uboldi C, Loudos G, Fragogeorgi E, Molinari V, Pucci A, Tsotakos T, Psimadas D, Ponti J, Franchini MC (2014) Targeted delivery of silver nanoparticles and alisertib: *in vitro* and *in vivo* synergistic effect against glioblastoma. Nanomedicine 9(6):839–849. https://doi.org/10.2217/nnm.14.1

Long TC, Saleh N, Tilton RD, Lowry GV, Veronesi B (2006) Titanium Dioxide (P25) produces reactive oxygen species in immortalized brain microglia (BV2): implications for nanoparticle neurotoxicity. Environ Sci Technol 40(14):4346–4352, PMID: 16903269

Lowell S, Shields JE, Thomas MA, Thommes M (2004) Characterization of porous solid and powders: surface area, pore size and density. Kluwer Academic Publisher, Dordrecht, ISBN 1-4020-2302-2 (HB), ISBN 1-4020-2303-0 (e-book)

Lu W, Xiong C, Zhang G, Huang Q, Zhang R, Zhang JZ, Li C (2009) Targeted photothermal ablation of murine melanomas with melanocyte-stimulating hormone analog-conjugated hollow gold nanospheres. Clin Cancer Res 15:876. https://doi.org/10.1158/1078-0432.CCR-08-1480

Lu Y, Wei J-Y, Yao D-S, Pan Z-M, Yao Y (2017) Application of carbon nanoparticles in laparoscopic sentinel lymph node detection in patients with early-stage cervical cancer. De Re V (ed) PLoS One. 12(9):e0183834. https://doi.org/10.1371/journal.pone.0183834

Lucky SS, Idris NM, Huang K, Kim J, Li Z, Thong PSP, Xu R, Soo KC, Zhang Y (2016) *In vivo* biocompatibility, biodistribution and therapeutic efficiency of titania coated upconversion nanoparticles for photodynamic therapy of solid oral cancers. Theranostics 6(11):1844–1865. https://doi.org/10.7150/thno.15088

Lundqvist M, Stigler J, Cedervall T, Berggard T, Flanagan MB, Lynch I, Elia G, Dawson K (2011) The evolution of the protein corona around nanoparticles: a test study. ACS Nano 5:7503–7509. https://doi.org/10.1021/nn202458g

Luo Y-L, Shiao Y-S, Huang Y-F (2011) Release of photoactivatable drugs from plasmonic nanoparticles for targeted cancer therapy. ACS Nano 5(10):7796–7804. https://doi.org/10.1021/nn201592s

Lynch I, Dawson KA (2008) Protein-nanoparticle interactions. Nano Today 3:40–47. https://doi.org/10.1016/S1748-0132(08)70014-8

Ma P, Xiao H, Li C, Dai Y, Chen Z, Hou Z, Lin J (2015) Inorganic carriers for platinum drug-delivery. Mater Today 18(10):554–564. https://doi.org/10.1016/j.mattod.2015.05.017

Mahmoudi M, Lynch I, Ejtehadi MR, Monopoli MP, Bombelli FB, Laurent S (2011) Protein-nanoparticle interactions: opportunities and challenges. Chem Rev 111:5610–5637. https://doi.org/10.1021/cr100440g

Maisel K, Ensign L, Reddy M, Cone R, Hanes J (2015) Effect of surface chemistry on nanoparticle interaction with gastrointestinal mucus and distribution in the gastrointestinal tract following oral and rectal administration in the mouse. J Control Release 197:48–57. https://doi.org/10.1016/j.jconrel.2014.10.026

Manke A, Wang L, Rojanasakul Y (2013) Mechanism of nanoparticle-induced oxidative stress and toxicity. BioMed Res Int, Article ID 942916, 15 pages. https://doi.org/10.1155/2013/942916

Marin E, Briceno MI, Caballero-George C (2013) Critical evaluation of biodegradable polymers used in nanodrugs. Int J Nanomedicine 8:3071–3091. https://doi.org/10.2147/IJN.S47186

McCarty MF, Barroso-Aranda J, Contreras F (2010) Oxidative stress therapy for solid tumors – a proposal. Med Hypotheses 74:1052–1054. https://doi.org/10.1016/j.mehy.2009.12.029

McDevitt MR, Chattopadhyay D, Kappel BJ, Jaggi JS, Schiffman SR, Antczak C, Njardarson JT, Brentjens R, Scheinberg DA (2007) Tumor targeting with antibody-functionalized, radiolabeled carbon nanotubes. J Nucl Med 48:1180–1189. https://doi.org/10.2967/jnumed.106.039131

Meadows KL, Hurwitz HI (2012) Anti-VEGF therapies in the clinic. Cold Spring Harb Perspect Med 2(10):a006577. https://doi.org/10.1101/cshperspect.a006577

Meddahi-Pellé A, Legrand A, Marcellan A, Louedec L, Letourneur D, Leibler L (2014) Organ repair, hemostasis, and in vivo bonding of medical devices by aqueous solutions of nanoparticles. Angew Chem Int Ed 53:6369–6373. https://doi.org/10.1002/anie.201401043

Melancon MP, Lu W, Yang Z, Zhang R, Cheng Z, Elliot AM, Stafford J, Olson T, Zhang JZ, Li C (2008) In vitro and in vivo targeting of hollow gold nanoshells directed at epidermal growth factor receptor for photothermal ablation therapy. Mol Cancer Ther 7(6):1730–1739. https://doi.org/10.1158/1535-7163.MCT-08-0016

Mendez R, Fernandes AR, Baptista BV (2017) Gold nanoparticle approach to the selective delivery of gene silencing in cancer – the case for combined delivery? Genes 8(94). https://doi.org/10.3390/genes8030094

Mestas J, Hughes CCW (2004) Of mice and not men: differences between mouse and human immunology. J Immunol 172:2731–2738, PMID 14978070

Minelli C, Lowe SB, Stevens MM (2010) Engineering nanocomposite materials for cancer therapy. Small 6(21):2336–2357. https://doi.org/10.1002/smll.201000523

Monopoli MP, Walczyk D, Campbell A, Elia G, Lynch I, Bombelli FB, Dawson KA (2011) Physical-chemical aspects of protein corona: relevance to *in vitro* and *in vivo* biological impact of nanoparticles. J Am Chem Soc 133:2525–2534. https://doi.org/10.1021/ja107583h

Moosavi MA, Sharifi M, Ghafary SM, Mohammadalipour Z, Khataee A, Rahmati M, Hajjaran S, Los MJ, Klonisch T, Ghavami S (2016) Photodynamic N-TiO_2 nanoparticle treatment induces controlled ROS-mediated autophagy and terminal differentiation of leukemia cells. Sci Rep 6, article number: 34413. https://doi.org/10.1038/srep34413

Mukherjee P, Bhattacharya R, Wang P, Wang L, Basu S, Nagy JA, Atala A, Mukhopadhyay D, Soker S (2005) Antiangiogenic properties of gold nanoparticles. Clin Cancer Res 11(9):3530–3534. https://doi.org/10.1158/1078-0432.CCR-04-2482

Muller J, Huaux F, Moreau N, Misson P, Heilier JF, Delos M et al (2005) Respiratory toxicity of multi-wall carbon nanotubes. Toxicol Appl Pharmacol 207:221–231. https://doi.org/10.1016/j.taap.2005.01.008

Müller K, Fedosov DA, Gompper G (2014) Margination of micro- and nano-particles in blood flow and its effect on drug delivery. Sci Rep 4:4871. https://doi.org/10.1038/srep04871

Murakami Y, Kenji E, Nosaka AY, Nosaka Y (2006) Direct detection of OH radicals diffused to the gas phase from the UV-irradiated photocatalytic TiO2 surfaces by means of laser-induced fluorescence spectroscopy. J Phys Chem B 110:16808–16811. https://doi.org/10.1021/jp063293c

Nel A, Xia T, Mädler L, Li N (2006) Toxic potential of materials at nanolevel. Science 311:622–627. https://doi.org/10.1126/science.1114397

Nguyen VH, Lee B-J (2017) Protein corona: a new approach for nanomedicine design. Int J Nanomed 12:3137–3151. https://doi.org/10.2147/IJN.S129300

Ni Y, Kan C, Gao Q, Wei J, Xu H, Wang C (2015) Heat generation and stability of a plasmonic nanogold system. J Phys D Appl Phys 49(5):055302. (9pp). https://doi.org/10.1088/0022-3727/49/5/055302

Nicomp 380 zeta potential user manual PSS-ZLSM-042106, 11/06

Niwa I, Hiura Y, Sawamura H, Iwai N (2008) Inhalation exposure to carbon black induces inflammatory responses in rats. Circ J 72:144–149. https://doi.org/10.1253/circj.72.144

Norton L, Massagué J (2006) Is cancer a disease of self-seeding? Nat Med 12(8):875–878. https://doi.org/10.1038/nm0806-875

Nosaka Y, Daimon T, Nosaka AY, Murakami Y (2004) Singlet oxygen formation in photocatalytic TiO_2 aqueous suspension. Phys Chem Chem Phys 6:2917–2918. https://doi.org/10.1039/B405084C

O'Neal DP, Hirsch LR, Halas NJ, Payne JD, West JL (2004) Photo-thermal tumor ablation in mice using near infrared-absorbing nanoparticles. Cancer Lett 209(2):171–176. https://doi.org/10.1016/j.canlet.2004.02.004

Oyarzun-Ampuero F, Guerrero A, Hassan-Lopez N, Morales JO, Bollo S, Corvalan A, Quest AFG, Kogan MJ (2015) Organic and inorganic nanoparticles for prevention and diagnosis of gastric cancer. Curr Pharm Design 21(29):145–154, PMID: 26323433

Oyewumi MO, Liu S, Moscow JA, Mumper RJ (2003) Specific association of thiamine-coated gadolinium nanoparticles with human breast cancer cells expressing thiamine transporters. Bioconjugate Chem 14(2):404–411. https://doi.org/10.1021/bc0340013

Park E-J, Park K (2008) Oxidative stress and pro-inflammatory responses induced by silica nanoparticles in vivo and in vitro. Toxicol Lett 184(2009):18–25. https://doi.org/10.1016/j.toxlet.2008.10.012

Park C, Youn H, Kim H, Noh T, Kook YH, Oh ET, Park HJ, Kim C (2009) Cyclodextrin-covered gold nanoparticles for targeted delivery of an anti-cancer drug. J Mater Chem 16. https://doi.org/10.1039/B816209C

Park SY, Chae SY, Park JO, Lee K, Park G (2016) Gold-conjugated resveratrol nanoparticles attenuate the invasion and MMP-9 and COX-2 expression in breast cancer cells. Oncol Rep 35(6):3248–3256. https://doi.org/10.3892/or.2016.4716

Peetla C, Vijayaraghavalu S, Labhasetwar V (2013) Biophysics of cell membrane lipids in cancer drug resistance: implications for drug transport and drug delivery with nanoparticles. Adv Drug Deliv Rev 65(0). https://doi.org/10.1016/j.addr.2013.09.004

Peinado H, Alečković M, Lavotshkin S, Matei I, Costa-Silva B, Moreno-Bueno G, Hergueta-Redondo M, Williams C, García-Santos G, Nitadori-Hoshino A, Hoffman C, Badal K, Garcia BA, Callahan MK, Yuan J, Martins VR, Skog J, Kaplan RN, Brady MS, Wolchok JD, Chapman PB, Kang Y, Bromberg J, Lyden D (2012) Melanoma exosomes educate bone marrow progenitor cells toward a pro-metastatic phenotype through MET. Nat Med 18(6):883–891. https://doi.org/10.1038/nm.2753

Peters K, Unger RE, Kirkpatrick CJ, Gatti AM, Monari E (2004) Effects of nano-scaled particles on endothelial cell function in vitro: studies on viability, proliferation and inflammation. J Mater Sci Mater Med 15(4):321–325, PMID: 15332593

Popescu T, Cremer L, Tudor M, AR Lupu (2016) ROS-mediated cytotoxicity and macrophage activation induced by TiO2 nanoparticles with Different in vitro non-cellular photocatalytic activities. South East Eur J Immunol, [S.l.] 2016:1–8. https://doi.org/10.3889/seejim.2016.20007

Pouw JJ, Ahmed M, Anninga B, Schuurman K, Pinder SE, Van Hemelrijck M, Pankhurst QA, Douek M, ten Haken B (2015) Comparison of three magnetic nanoparticle tracers for sentinel lymph node biopsy in an in vivo porcine model. Int J Nanomed 10:1235–1243. https://doi.org/10.2147/IJN.S76962

Prado-García H, Sánchez-García FJ (2017) Immuno-metabolism in tumor microenvironment. Front Immunol 8, Article 374. https://doi.org/10.3389/fimmu.2017.00374

Pramanik M, Song KH, Swierczewska M, Green D, Sitharaman B, Wang LV (2009) In vivo carbon nanotube-enhanced non-invasive photoacoustic mapping of the sentinel lymph node. Phys Med Biol. 54(11):3291–3301. https://doi.org/10.1088/0031-9155/54/11/001

Qian Y, Qiu M, Wu Q, Tian Y, Zhang Y, Gu N, Li S, Xu L, Yin R (2014) Enhanced cytotoxic activity of cetuximab in EGFR-positive lung cancer by conjugating with gold nanoparticles. Sci Rep 4, Article number 7490. https://doi.org/10.1038/srep07490

Rahman M, Laurent S, Tawil N, Yahia L, Mahmoudi M (2013) Protein-nanoparticle interactions. The bio-nano interface. Springer, X 84p 24 illus, 20 illus, hardcover, ISBN: 978-3-642-37554-5

Ramires PA, Romito A, Cosentino F, Milella E (2001) The influence of titania/hydroxyapatite composite coatings on in vitro osteoblasts behaviour. Biomaterials 22(12):1467–1474, PMID:11374445

Rau JL (2005) The inhalation of drugs, advantages and problems. Respir Care 5(3):367–382, PMID:15737247

Reddy L, Arias JL, Nicolas J, Couvreur P (2012) Magnetic nanoparticles: design and characterization, toxicity and biocompatibility, pharmaceutical and biomedical applications. Chem Rev 112:5818–5878. https://doi.org/10.1021/cr300068p

Rocha-Lima CM, Soares HP, Raez LE, Singal R (2007) EGFR targeting of solid tumors. Cancer Control 14(3):295–304. https://doi.org/10.1177/107327480701400313

Roma-Rodrigues C, Raposo LR, Cabral R, Paradinha F, Baptista PV, Fernandes AR (2017) Tumor microenvironment modulation via gold nanoparticles targeting malicious exosomes: implications for cancer diagnostics and therapy. Int J Mol Sci 18:162. https://doi.org/10.3390/ijms18010162

Rose S, Prevoteau A, Elzière P, Hourdet D, Marcellan A, Leibler L (2014) Nanoparticle solutions as adhesives for gels and biological tissues. Nature 505:382–385. https://doi.org/10.1038/nature12806

Rosensweig RE (2002) Heating magnetic fluid with alternating magnetic field. J Magn Magn Mater 252:370–374. https://doi.org/10.1016/S0304-8853(02)00706-0

Rothenberger G, Moser J, Graetzel M, Serpone N, Sharma DK (1985) Charge carrier trapping and recombination dynamics in small semiconductor particles. J Am Chem Soc 107(36):8054–8059

Rozhkova EA, Ulasov I, Lai B, Dimitrijevic NM, Lesniak MS, Rajh T (2009) A high-performance nanobio photocatalyst for targeted brain cancer therapy. Nano Lett *9*(9):3337–3342. https://doi.org/10.1021/nl901610f

Saraiva C, Praça C, Ferreira R, Santos T, Ferreira L, Bernardino L (2016) Nanoparticle-mediated brain drug delivery: overcoming blood–brain barrier to treat neurodegenerative diseases. J Control Release 235:34–47. https://doi.org/10.1016/j.jconrel.2016.05.044

Sasaki T, Hiroki K, Yamashita Y (2013) The role of epidermal growth factor receptor in cancer metastasis and microenvironment. Biomed Res Int 2013:546318. https://doi.org/10.1155/2013/546318

Schneider CS, Xu Q, Boylan NJ, Chisholm J, Tang BC, Schuster BS, Henning A, Ensign LM, Lee E, Adstamongkonkul P, Simons BW, Wang S-Y S, Gong X, Yu T, Boyle MP, Suk JS, Hanes J (2017) Nanoparticles that do not adhere to mucus provide uniform and long-lasting delivery to airways following inhalation. Sci Adv 3:e1601556. https://doi.org/10.1126/sciadv.1601556

Schuster TM (2000) On-line biophysics textbook, volume: separations and hydrodynamics, chapter 1 – survey of biomolecular hydrodynamics. www.biophysics.org/Portals/1/PDFs/Education/vbloomfield.pdf

Senger DR, Galli SJ, Dvorak AM, Perruzzi CA, Harvey VS, Dvorak HF (1983) Tumor cells secrete a vascular permeability factor that promotes accumulation of ascites fluid. Science 219 (4587):983–985, PMID:6823562

Sershen SR, Westcott SL, West JL, Halas NJ (2001) An opto-mechanical nanoshell–polymer composite. Appl Phys B 73:379–381. https://doi.org/10.1007/s003400100689

Sharma A, Madhunapantula SRV, Robertson GP (2013) Toxicological considerations when creating nanoparticle based drugs and drug delivery systems? Expert Opin Drug Metab Toxicol 8 (1):47–69. https://doi.org/10.1517/17425255.2012.637916

Simberg D, Park JH, Karmali PP, Zhang WM, Merkulov S, McCrae K, Bhatia SN, Sailor M, Rouslahti E (2009) Differential proteomics analysis of the surface heterogeneity of dextran iron oxide nanoparticles and the implications for their *in vivo* clearance. Biomaterials 30:3926–3933. https://doi.org/10.1016/j.biomaterials.2009.03.056

Singh AK (2015) Engineered nanoparticles, structure, properties and mechanisms of toxicity. In: Chapter 6: nanoparticle pharmacokinetics and toxicokinetics. Academic Press, Amsterdam, pp 230–296

Smith L, Kuncik Z, Ostrikov K, Kumar S (2012) Nanoparticles in cancer imaging and therapy. J Nanomater, Article ID 891318, 7 pages. https://doi.org/10.1155/2012/891318

Solanki A, Kim JD, Lee K-B (2008) Nanotechnology for regenerative medicine: nanomaterials for stem cell imaging. Nanomedicine 3(4):567–578. https://doi.org/10.2217/17435889.3.4.567

Spiliopoulos K, Peschos D, Batistatou A, Ntountas I, Agnantis N, Kitsos G (2015) Vasculogenic mimicry: lessons from melanocytic tumors. In Vivo 29(3):309–317, PMID: 25977376

Steinman RM, Mellman I (2004) Immunotherapy: bewitched, bothered and bewildered no more. Science 305:197–200. https://doi.org/10.1126/science.1099688

Szabo E (2006) Selecting targets for cancer prevention: where do we go from here, nature reviews. Cancer 6:867–874. https://doi.org/10.1038/nrc2008

Takanashi S, Hara K, Aoki K, Usui Y, Shimizu M, Haniu H et al (2012) Carcinogenicity evaluation for the application of carbon nanotubes as biomaterials in rasH2 mice. Sci Rep 2:498. https://doi.org/10.1038/srep00498

Toy R, Hayden E, Shoup C, Baskaran H, Karathanasis E (2011) Effect of particle size, density and shape on margination of nanoparticles in microcirculation. Nanotechnology 22(11):115101, PMCID: PMC3530262

Toy R, Peiris PM, Ghaghada KB, Karathanasis E (2014) Shaping cancer nanomedicine: the effect of particle shape on the in vivo journey of nanoparticles. Nanomedicines (Lond) 9(1):121–134. https://doi.org/10.2217/nnm.13.191

Uchechi O, Ogbonna JDN, Attama AA (2014) Nanoparticles or dermal and transdermal drug delivery, application of nanotechnology in drug delivery. InTech:193–235. https://doi.org/10.5772/58672

Vallée A, Guillevin R, Vallée J-N (2018) Vasculogenesis and angiogenesis initiation under normoxic conditions through Wnt/β-catenin pathway in gliomas. Rev Neurosci 29(1):71–91. https://doi.org/10.1515/revneuro-2017-0032

van der Vos KE, Balaj L, Skog J, Breakefield XO (2011) Brain tumor microvesicles: insights into intercellular communication in the nervous system. Cell Mol Neurobiol 31(6):949–959. https://doi.org/10.1007/s10571-011-9697-y

van der Worp HB, Howells DW, Sena ES, Porritt MJ, Rewell S, O'Collins V, Macleod MR (2010) Can animal models of disease reliably inform human studies? PLoS One 7(3):e1000245. https://doi.org/10.1371/journal.pmed.1000245

Verma P, Thakur AS, Deshmukh K, Jha AK, Verma S (2010) Routes of drug administration. IJPSR 1(1):54–59, E-ISSN 2229-4619

Vroman L, Adams AL, Fischer GC, Munoz PC (1980) Interaction of high molecular weight kininogen, factor-Xii, and fibrinogen in plasma at interfaces. Blood 55:156–159, PMID:7350935

Wang B, He X, Zhang Z, Zhao Y, Feng W (2012a) Metabolism of nanomaterials in vivo: blood circulation and organ clearance. Acc Chem Res 46(3):761–769. https://doi.org/10.1021/ar2003336

Wang X, Guo J, Chen T, Nie H, Wang H, Zang J et al (2012b) Multi-walled carbon nanotubes induce apoptosis via mitochondrial pathway and scavenger receptor. Toxicol In Vitro 26:799–806. https://doi.org/10.1016/j.tiv.2012.05.010

Wang Y, Huang H-Y, Yang L, Zhang Z, Ji H (2016) Cetuximab-modified mesoporous silica nanomedicine specifically targets EGFR-mutant lung cancer and overcomes drug resistance. Sci Rep 6, article number 25468. https://doi.org/10.1038/srep25468

Wangeblast E, Soto M, Gutièrrez-Angel HCA, Gable AL, Macell AR, Erard N, Wlliams AM, Kim SY, Dickopf S, Harrell JC, Smith AD, Perou CM, Wilkinson JE, Hannon GJ, Knott SRV (2015) A model of breast cancer heterogeneity reveals vascular mimicry as a driver of metastasis. Nature 520:358–362. https://doi.org/10.1038/nature14403

Weinstein IB, Joe AK (2006) Mechanisms of Disease: oncogene addiction – a rationale for molecular targeting in cancer therapy. Nat Clin Pract Oncol 3(8):448–457. https://doi.org/10.1038/ncponc0558

Weissleder R, Nahrendorf M, Pittet MJ (2014) Imaging macrophages with nanoparticles. Nat Mater 13:125–138. https://doi.org/10.1038/nmat3780

Widakowich C, de Gastro G Jr, de Azambyra E, Dinh P, Awada A (2007) Side effects of approved molecular targeted therapies in solid cancers. Oncologist 12:1443–1455. https://doi.org/10.1634/theoncologist.12-12-1443

Wildeboer RR, Southern P, Pankhurst QA (2014) On the reliable measurement of specific absorption rates and intrinsic loss parameters in magnetic hyperthermia materials. J Phys D Appl Phys 47(49):14

Williams DF (2008) On the mechanisms of biocompatibility. Biomaterials 29:2941–2953. https://doi.org/10.1016/j.biomaterials.2008.04.023

Wimpenny I, Markides H, El Haj AJ (2012) Orthopaedic applications of nanoparticle-based stem cell therapies. Stem Cell Res Therapy 3:13. https://doi.org/10.1186/scrt104

Winkler HC, Suter M, Naegeli H (2016) Critical review of the safety assessment of nano-structured silica additives in food. J Nanobiotechnol 14:44. https://doi.org/10.1186/s12951-016-0189-6

Winter M, Beer H-D, Hornung V, Krämer U, Schins RFP, Förster I (2011) Activation of the inflammasome by the amorphous silica and TiO_2 nanoparticles in murine dendritic cells. Nanotoxicology 5:326–340. https://doi.org/10.3109/17435390.2010.506957

Winter A, Woekhaus J, Wawoschek F (2014) A novel method for intraoperative sentinel lymph node detection in prostate cancer patients using superparamagnetic iron oxide nanoparticles and a handheld magnetometer: the initial clinical experience. Ann Surg Oncol 21:4390–4396. https://doi.org/10.1245/s10434-014-4024-8

World Health Organization, Media Centre, Cancer, February (2017). http://www.who.int/mediacentre/factsheets/fs297/en/. Accessed 17 Jan 2017

Wu X, Lin Q, Chen G, Lu J, Zeng Y, Chen X, Yan J (2015) Sentinel lymph node detection using carbon nanoparticles in patients with early breast cancer. PLoS One 10(8):e0135714. https://doi.org/10.1371/journal.pone.0135714

Xie J, Pan X, Wang M, Yao L, Liang X, Ma J, Fei Y, Wang PN, Lan M (2016) Targeting and photodynamic killing of cancer cell by nitrogen-doped titanium dioxide coupled with folic acid. Nanomaterials 6:113. https://doi.org/10.3390/nano6060113

Xu XF, Gu J (2016) The application of carbon nanoparticles in the lymph node biopsy of cN0 papillary thyroid carcinoma: a randomized controlled clinical trial. Asian J Surg. https://doi.org/10.1016/j.asjsur.2015.11.004

Yan J, Xue F, Chen H, Wu X, Zhang H, Chen G, Lu J, Cai L, Xiang G, Deng Z, Zheng Y, Zheng X, Li G (2014) A multi-center study of using carbon nanoparticles to track lymph node metastasis in T1-2 colorectal cancer. Surg Endosc 28(12):3315–3321. https://doi.org/10.1007/s00464-014-3608-5

Yao C, Zhang L, Wang J, He Y, Xin J, Wang S, Xu H, Zhang Z (2016) Gold nanoparticle mediated phototherapy for cancer, Hindawi Publishing Corporation. J Nanomater, Article ID 5497136, 29 pages, https://doi.org/10.1155/2016/5497136

Yildirimer L, Thanh NTK, Loizidou M, Seifalian AM (2011) Toxicology and clinical potential of nanoparticles. NanoToday 6(6):585–607. https://doi.org/10.1016/j.nantod.2011.10.001

Yokoyama T, Tam J, Kuroda S, et al (2011) EGFR-targeted hybrid plasmonic magnetic nanoparticles synergistically induce autophagy and apoptosis in non-small cell lung cancer cells. Basu S (ed) PLoS One 6(11):e25507. https://doi.org/10.1371/journal.pone.0025507

You DG, Deepagan VG, Um W, Jeon S, Son S, Chang H, Yoon HI, Cho YW, Swierczewska M, Lee S, Pomper MG, Kwon IC, Kim K, Park JH (2016) ROS-generating TiO_2 nanoparticles for non-invasive sonodynamic therapy of cancer. Sci Rep 6, Article number 23200. https://doi.org/10.1038/srep23200

Yu W, Cao XL, Xu G, Song Y, Li G, Zheng H (2016) Potential role for carbon nanoparticles to guide central neck dissection in patients with papillary thyroid cancers. Surgery 160 (3):755–761. https://doi.org/10.1016/j.surg.2016.04.017

Zhang A-P, Sun Y-P (2004) Photocatalytic killing effect of TiO_2 nanoparticles on Ls-174-t human colon carcinoma cells. World J Gastroenterol 10(21):3191–3193, PMID: 15457572

Zhang XD, Wu D, Shen X, Liu P-X, Yang N, Zhao B, Zhang H, Sun Y-M, Zhang L-A, Fan F-Y (2011a) Size dependent in vivo toxicity of PEG-coated gold nanoparticles. Int J Nanomedicine 6:2071–2081. https://doi.org/10.2147/IJN.S21657

Zhang XQ, Lam R, Xu X, Chow EK, Kim HJ, Ho D (2011b) Multimodal nanodiamond drug delivery carriers for selective targeting, imaging, and enhanced chemotherapeutic efficacy. Adv Mater 23(41):4770–4775. [PubMed: 21932280] 28

Zhang Y, Deng J, Zhang Y, Guo F, Li C, Zou Z et al (2013) Functionalized single-walled carbon nanotubes cause reversible acute lung injury and induce fibrosis in mice. J Mol Med (Berl) 91 (1):117–128. https://doi.org/10.1007/s00109-012-0940-x

Zhang L, Li Y, Yu JC (2014) Chemical modification of inorganic nanostructures for targeted and controlled drug delivery in cancer treatment. J Mater Chem 2:452. https://doi.org/10.1039/C3TB21196G

Zitoogel L, Tesniere A, Kroemer G (2006) Cancer despite immunosurveillance: immunoselection and immunosubversion. Nat Rev Immunol 6:715–727. https://doi.org/10.1038/nri1936

Chapter 3
Modification of Oligomers and Reinforced Polymeric Composites by Carbon Nanotubes and Ultrasonic

Aleksandr Evhenovych Kolosov and Elena Petryvna Kolosova

Contents

3.1 Introduction: Modification as Basic Direction of Improving the Technological and Operational Characteristics of Classical and Nanomodified Liquid Polymeric Media and Reinforced Polymeric Composites . . . 91
3.2 Physical Modification of Liquid Polymeric Media and Reinforced Polymeric Composites: Methods and Means . . . 93
  3.2.1 Physical Modification of Liquid Polymeric Media by Ultrasonic . . . 93
  3.2.2 Ultrasonic Modification of Reinforced Polymeric Composites . . . 94
  3.2.3 Technical Means for Ultrasonic Modification . . . 94
  3.2.4 Process Design for the Production of Classical and Nanomodified Composites with Ultrasonic Modification . . . 96
3.3 Modification of Oligomers and Reinforced Polymeric Composites by Carbon Nanotubes . . . 97
  3.3.1 Bulk Content of a Nanofiller in a Polymer Composite . . . 97
  3.3.2 Chemical Modification of CNT . . . 97
  3.3.3 Preparation of Carbon Nanomaterial Dispersions in Organic Solvents and Rubber . . . 99
3.4 Preparation and Study of Epoxide Nanocomposites . . . 99
  3.4.1 Features of Nanocarbon Modification of Epoxide Oligomers . . . 100
  3.4.2 Roller Dispersion of Highly Viscous Suspensions of Epoxide Oligomers with CNT . . . 103
  3.4.3 Solidified Nanomodified Oligomers Microstructure . . . 106
3.5 Use of Carbon Nanotubes to Improve the Physico-mechanical and Operational Characteristics of Polymers . . . 107

A. E. Kolosov (✉)
Chemical, Polymeric and Silicate Machine Building Department of Chemical Engineering Faculty, National Technical University of Ukraine, «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine
http://www.kolosov.ua

E. P. Kolosova
Physics and Mathematics Faculty, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_3

3.5.1 Use of Carbon Nanotubes to Increase the Strength and Heat Resistance of Epoxide Binders 108
3.5.2 Fatigue Characteristics of Polymer Nanocomposite Materials 109
3.5.3 Electrical Conductivity of Polymer Composite Materials Modified by Carbon Nanotubes 110
3.6 Conclusions 112
References 113

Abstract The modern development of mankind is inextricably linked with the improvement of existing thermoplastics and thermosets, as well as the creation of new polymers, for example, nanomodified polymer composite materials, with new operational properties. The main problematic situations that occur in the development of these polymeric composite materials are obtaining of defect-free composite structures, practically without air inclusions, a uniform distribution of the reinforcing filler over the cross-section of the composite to ensure the completeness of the properties of the constituent components of the composite, and also to improve the properties of the components of which the composite consists. At the same time, a "cementing" role is assigned to the polymer matrix in the structure of the composite, which determines the direction of improvement of its structural, technological, and operational properties, for example, by modification. At present, the modification (physical as ultrasonic, chemical, and physicochemical) is the basic direction of improving the technological and operational characteristics of classical and nanomodified polymer composite materials. For nanomodified polymer composite materials, the need to deagglomerate and uniformly disperse nanomodifiers, for example, carbon nanotubes, in a liquid polymer matrix is added to the above problematic situations. This is due to the fact that these nanomodifiers due to their physical nature in the initial state are prone to aggregation, thereby impairing the properties of the final nanocomposite into which they are incorporated. Equally important is the design of technology and equipment for energy- and resource-saving, as well as highly productive molding of composites with predetermined properties.

We reviewed that ultrasonic modification is widely used in many branches of industry and technology, for example, in chemical engineering for molding both thermosetting plastics and thermoplastics. The achievement of the necessary positive result from the cavitation effect in liquid polymeric media can be attained by varying the parameters of the cavitation treatment (frequency, amplitude, intensity, pressure, temperature, volume of the liquid medium being treated). The total height of the epoxy composition lift (the productivity of ultrasonic impregnation) in the impregnation of fibrous fillers with previously sonificated epoxy composition increases by 2.5–3 times. Ultrasonic treatment allows to increase the deformation-strength and adhesion characteristics of materials, to lower the level of residual stresses, to increase the durability, and, moreover, to significantly shorten the hardening time. Also low-frequency ultrasonic treatment is one of the most effective methods for distributing carbon nanotubes evenly in a polymer matrix. It was investigated that nanomodifiers lead to improved tensile strength and deformation, fatigue strength, electrical conductivity, and glass transition temperature. For example, we investigated that the strength of nanomodified polymer composite materials is lead to improved due to an insignificant (8%) increase of the elasticity modulus and a considerable (25%) increase of the fracture strength (8%) of the studied nanocomposites. It was showed that the physico-mechanical characteristics improved after nanomodification of an epoxy binders by an average of (20–30)%; the compression strength limit and heat resistance, by 70%. The destructive load of fiberglass increased by 2–3 times. Also the complexity of solving the problem of designing a technology and equipment for the production of classical reactoplastic polymer composite material is due to the need to investigate a set of issues, concerning with studying the interrelations between the structural, mechanical, and geometric parameters of products, on the one hand, and the technological factors of their production, on the other hand.

Keywords Reactoplast · Oligomer · Composite · Filler · Carbon nanotube · Modification · Ultrasonic · Cavity · Production · Properties

Abbreviations

CNM	Carbon nanomaterial
CNT	Carbon nanotube
EO	Epoxy (epoxide) oligomer
EB	Epoxy (epoxide) binder
EC	Epoxy (epoxide) composition
EP	Epoxy polymer
PCM	Polymer composite material
NM	Nanomodified
NM PCM	Nanomodified polymer composite material
MWCNT	Multi-walled carbon nanotube
US	Ultrasonic

3.1 Introduction: Modification as Basic Direction of Improving the Technological and Operational Characteristics of Classical and Nanomodified Liquid Polymeric Media and Reinforced Polymeric Composites

In the last two and a half decades, nanotechnology has been actively developed all over the world. With respect to traditional and nanomodified polymers and reinforced polymeric composites based on them, modification methods are considered as a basic direction of improving their technological and operational characteristics. At present, the modification (physical as ultrasonic – US, chemical, and physicochemical) is the basic direction of improving the technological and operational characteristics of classical and nanomodified (NM) elastomers and reinforced polymer composite materials (PCM) based on them (Harris 2004; Kolosov 2014a).

Of the same importance are the design issues of the technological process of producing classical and NM polymer composite materials (NMPCM) (Kolosov 2015a). In this case, the use of US modification and intensification is the main method of increasing the productivity of the process and improving the performance characteristics of such materials (Kolosov et al. 2012a, 2014b).

PCM-containing carbon nanomaterials (CNM), in particular, carbon nanotubes (CNTs), have been researched since the end of the 1990s, when these materials became available in relatively large quantities (Harris 2004). Such studies are much rarer than those dedicated to the use of fullerene. However, interesting practical results have been obtained (Aldoshin 2008). Many processing and operational characteristics of elastomers and liquid polymers can be increased considerably (sometimes several times) by modifying them with small amounts of nanoparticles, e.g., fullerenes, nanotubes, nanowires, inorganic nanoparticles, etc. (Karpacheva 2000; Wang et al. 2004; Badamshina and Gafurova 2008; Luzgarev et al. 2013; Kondrashov et al. 2013). For this, effective methods for dispersing CNT in organic solvents and liquid polymeric media are required.

A number of studies have been devoted to the preparation, enhancement of operational properties, and the use of reactoplastic NMPCM. In particular, the prospects for development and practical application of nanotechnology, including for production of NMPCM, were analyzed in terms of the achievements of modern science and technology (Kolosov 2015a). Effective technical means (methods and devices) designed to produce reactoplastic NMPCM that provide increased strength and service life for structures based on them were analyzed (Kolosov 2016a). Effective methods for dispersing CNT in organic solvents and liquid polymeric media were analyzed (Kolosov 2016b).

Features and problems of producing reactoplastic NMPCM were considered using modification of epoxide oligomers with CNT as an example (Kolosov 2016c). The characteristics of reactoplastic NMPCM were analyzed using structural carbon fiber prepregs as examples (Kolosov 2017).

The results obtained both in the abovementioned and in other studies provide prerequisites for further studies on the improvement of effective methods for the modification of classical and NM liquid polymer media and reinforced PCM based on them. The abovementioned aspects are briefly described in this chapter.

3.2 Physical Modification of Liquid Polymeric Media and Reinforced Polymeric Composites: Methods and Means

3.2.1 Physical Modification of Liquid Polymeric Media by Ultrasonic

As the main method of physical modification of liquid polymer media and reinforced PCM based on them, US low-frequency cavitation is currently used. At the same time, the achievement of the necessary positive result from the cavitation effect can be achieved by varying the parameters of the cavitation treatment (frequency, amplitude, intensity, pressure, temperature, volume of the liquid medium being treated).

On the other hand, the hardening value depends on the particular type of oligomer to be processed and can be up to 40–50% for classical thermosets or several times (depending on the type of nanomodifier) for nanomodified reactoplastics (Kolosov 2014c, 2016c). The effect of low-frequency US treatment regimes on reactoplastic PCM operating properties was analyzed. An example was provided for effective US treatment by the technology developed compared with known methods (Kolosov 2014c).

The analysis of the specific features of the realization of US modification of liquid media indicates that it is promising to carry out such a modification of liquid epoxy oligomers (EO) and epoxy compositions (EC) used in the molding of reactoplastic PCM. Moreover, such a modification is effective both in the low-frequency and mid-frequency US ranges.

The effect of heterofrequency US treatment on reactoplastic PCM operating properties was analyzed. It was established established for effective process parameters of heterofrequency US cavitation in liquid EC, and this makes it possible to select effective energy-saving processing base parameters for preparing epoxy polymers (EP) based upon them (Kolosov 2014d).

The use of excessive pressure in the US treatment of liquid polymeric media, for example, during the molding of epoxy muffs with shape memory effect, is an important factor in increasing the intensity and shortening the processing time, as well as the cumulative production time of the finished product. The effect of low-frequency US treatment regime and excess pressure on reactoplastic PCM (unfilled and filled with short-fiber fillers) is analyzed. Optimum process parameters are established for US treatment of liquid epoxy composites (Kolosov 2014e).

These effective parameters, as a rule, are set experimentally in each specific case. The found optimal parameters of US cavitation processing lead to an increase in the physico-mechanical properties of solidified oligomers (Harris 2004; Karimov et al. 1989).

3.2.2 Ultrasonic Modification of Reinforced Polymeric Composites

Effective US modification of reinforced polymeric composites allows to achieve several results at once. Firstly, there is US activation of the surface and structure of the fibrous filler to improve its wettability with EC. Secondly, there is degassing of the structure of the filler just before it is impregnated. Thirdly, there is an increase in the productivity of the impregnation process and the dosed application of the EC by increasing the speed of pulling the filler while preserving the properties of the final composite. Finally, the use of US is an effective method of stabilizing the content of epoxy binder in impregnated woven filler, with variation in the speed of its stretching during the dosing process.

It has been experimentally established that as a result of the application of effective US treatment regimes in the impregnation of oriented fibrous fillers, the total height of the EC lift (the productivity of US impregnation) in the impregnation of fibrous fillers with previously sonificated EC increases by 2.5–3 times (Kolosov et al. 1989). In addition, US treatment allows to increase the deformation-strength and adhesion characteristics of materials, to lower the level of residual stresses, to increase the durability, and, moreover, to significantly shorten the hardening time (Kolosov et al. 1990).

Technological bases of impregnation of fibrous fillers and dosed application of epoxy binders on them with application of US were developed. Improved high-performance designs of impregnation and dosing unit on serial impregnating and drying equipment. It is established that the use of the developed energy-saving and environmentally safe technical means makes it possible to utilize highly viscous and highly concentrated impregnating compounds. In addition, quality is increased and the productivity of the impregnation process is increased, and uniform impregnated PCM is obtained practically without air inclusions.

It is these factors that determine the choice of US as the dominant method of physical modification of fibrous PCM at the main stages of their production.

3.2.3 Technical Means for Ultrasonic Modification

US modification is widely used in many branches of industry and technology, for example, in chemical engineering for molding both thermosetting plastics and thermoplastics. Some examples of the application of US modification are presented by repair and restoration technologies of polyethylene gas pipelines. Aspects of connection and restoration of polymeric pipelines for gas transport from the point of view of efficiency of US modification and heat shrinkage are studied in Kolosov et al. (2011a). Production bases for molding of epoxy repair couplings with shape memory are represented in Kolosov et al. (2011b). Analysis of surface treatment methods for polyethylene pipes connected by banding and low US treatment is presented in the study done by Kolosov et al. (2011c). Characteristics of practical implementation of production bases developed using epoxy glue compositions and banding are investigated in Kolosov et al. (2011d). Aspects of thermistor couplings and components used in gas pipeline repair with US treatment are presented in Kolosov et al. (2011e).

Existing technical means for US modification of liquid, in particular, polymer media, and reinforcing fillers on their basis can be conditionally divided into US concentrators – speed transformers and radiating plates. The first type of US equipment is used primarily for processing liquid polymer media, including when nanomodifiers are incorporated into them. The second type of US technical means is used primarily for processing the impregnated woven fibrous fillers. For both types of US technical means, it is necessary to determine the effective design and technological parameters (Kolosov 2012b).

The first type of radiators has been studied quite fully, while a number of problems arise in calculating the second type of US technical means. When using powerful emitters used in various technological processes, first of all, it is necessary to control the level of intensity. Otherwise, such undesirable changes as mechanical destruction, chemical reactions, etc. can occur in the liquid medium being treated. In addition, the level of intensity and frequency of oscillations must meet the sanitary standards and requirements of the technology used. In this regard, it is advisable to analyze the effective technical means of cavitation processing with a radiating plate that generates US vibrations necessary for specific technological processes, as well as corresponding improved methods for calculating these technical means.

The existing unevenness of bending vibrations under the action of an US field along and across the outer surface of the radiating plate makes it difficult to rationally use US transducers in automated technological installations. This is particularly evident in the contact treatment of woven materials of considerable width. As a result, the appearance of defective portions of the resulting final PCM is possible.

Analytical peculiarities of US cavitators based on piezoceramic transducers with a radiative plate, which experiences bending vibrations, are analyzed. The acoustic dimensions of components of a sectional piezoelectric transducer used in the production process of contact US treatment of a dry 1120-mm-wide cloth impregnated with a polymeric binder are calculated (Kolosov et al. 2013). The approaches developed by the authors to determine the effective design and technological parameters make it possible to eliminate the nonuniformity of the above-bending vibrations (Kolosov et al. 2012b, 2013). The implementation of the developed approaches allows to obtain practically defect-free classical PCM and NMPCM.

3.2.4 Process Design for the Production of Classical and Nanomodified Composites with Ultrasonic Modification

The complexity of solving the problem of designing a technology and equipment for the production of reactoplastic PCM is due to the need to investigate a set of issues. These issues are aimed at identifying and studying the interrelations between the structural, mechanical, and geometric parameters of products, on the one hand, and the technological factors of their production, on the other hand. The subject of researching the technology of manufacturing products from PCM is the patterns that establish not only the interrelations but also the mutual influence of technological factors. The latter determine in certain pre-defined production conditions the production of the required performance characteristics of manufactured products from PCM within the limits of design deviations.

Thus, for example, the kinetic equations of longitudinal and transverse impregnation of oriented fibrous fillers with polymeric binders make it possible to predict the speed of broaching the fibrous filler through the impregnating bath and also to design its dimensions (Kolosov 1988). The study of the influence of technological impregnation regimes on the strength of impregnated and cured fibrous fillers makes it possible to design the optimum force of impregnated fibrous fillers during winding (Kolosov et al. 1988; Kolosov and Repelis 1989).

To minimize material and time costs, it is necessary to use effective approaches for modeling the design and technological parameters of technology and equipment (tools) constructions for the production of reactoplastic PCM. This should be done taking into account the specifics of the objects being modeled, in particular, by adapting the perspective methodology of structural-parametric modeling to solve specific problems (Kolosov et al. 2015). The principle of the system approach assumes the analysis of the investigated object simultaneously and as a set of certain interrelated elements and as a potential component of the higher hierarchical level. Therefore, it seems expedient to separate the investigated structural scheme of the impregnation and dosing application of the polymer binder onto a long fibrous filler using US into separate structured blocks.

These blocks represent the corresponding base processes, and in this case include (1) US treatment unit for EO and preparation of impregnating composition (EC), (2) a block of "free" impregnation of oriented fiber filler with liquid EC, and (3) a block of dosed application of liquid EC to impregnated fibrous filler. In the future, only the above-enlarged blocks and their constituent structural elements are analyzed, as well as the interrelations between them, within the framework of the synthesis.

It should be noted that research and modeling of the full technological cycle for obtaining high-strength and defect-free classical PCM and NMPCM and the entire complex of equipment realizing it, are extremely difficult tasks that have not yet been solved.

3.3 Modification of Oligomers and Reinforced Polymeric Composites by Carbon Nanotubes

3.3.1 Bulk Content of a Nanofiller in a Polymer Composite

Even small additions of CNT (1–2%, sometimes 0.1–0.3%) can increase by several times the elasticity modulus and tensile strength of a reactoplastic polymer (Coleman et al. 2006). The thermal and electrical conductivity of the polymer is sharply increased at the same time. CNT additives can also expand the operating temperature range of NMPCM by increasing the glass-transition temperature T_g (Aldoshin 2008).

The conditions required to produce NMPCM are a small size and CNM particle distribution as uniform as possible in the polymeric matrix. The tendency of CNM to aggregate hinders the preparation of stable CNT dispersions in water and organic solvents (including polymers). Therefore, effective methods for facilitating aggregate disintegration are being actively pursued (Atovmyan et al. 2005). These include chemical modification of CNM by low-molecular-mass compounds and polymers to form covalent bonds between the modifier and CNT and non-covalent modification of CNM by both low-molecular-mass and polymeric surfactants.

Polymethyl methacrylate was used as an example (Aldoshin 2008) to illustrate that small additives (10^{-2}–10^{-3} wt.%) of carboxylated multi-walled CNT (MWCNT) to the starting reaction mixture can increase the dynamic elasticity modulus of the polymers by 1.5–2 times. The yield (change of sample linear dimension) of the polymers decreases by ~3 times on passing the glass-transition temperature T_g. The effect reaches a maximum at MWCNT concentrations of ~0.05 wt.%.

Thus, a serious scientific effort to study and design new NMPCM with improved operational characteristics as compared with the starting polymers was undertaken. This helped to extend the service life (and decrease the materials consumption, mass, and dimensions) of parts prepared from NMPCM (Aldoshin 2008).

3.3.2 Chemical Modification of CNT

Practical application of CNT is hindered by their insolubility (in particular, in aqueous media) and tendency to aggregate and form linkages, channels, etc. (Priluts'ka et al. 2009). Aggregates form because of the hydrophobicity of the CNT and the action of intratubular forces, e.g., van Der Waals and electrostatic interactions.

Various chemical modification methods (oxidation, non-covalent, and covalent functionalization) and US action are used to improve the properties of colloidal CNT dispersions (Smart et al. 2006; Hirsch 2002). For example, oxidation of CNT by various acids forms CNT with carbonyls and/or carboxylic acids on the CNT ends and walls (Prylutska et al. 2008). However, such modification can alter the CNT properties. Ultrasonication of their aqueous suspensions, a commonly employed method for altering CNT solubility, is used for accelerated dispersion of CNT (Andrews et al. 2002).

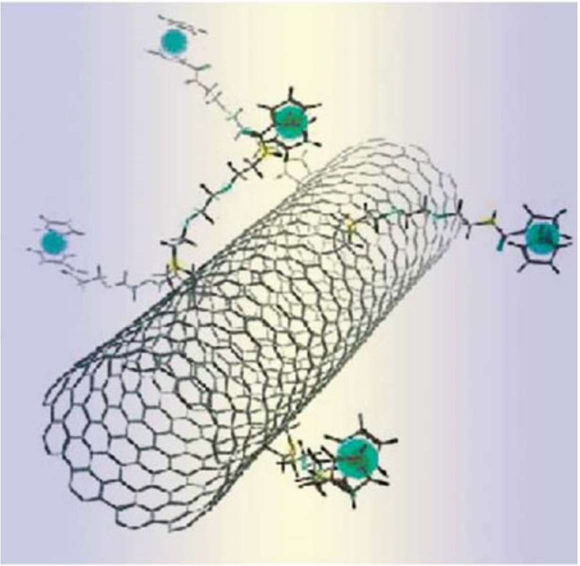


Fig. 3.1 Diagram of single-walled CNT functionalized by organic compounds (Priluts'ka et al. 2009). (Modified after Priluts'ka et al. 2009)

A unique method for chemical modification of CNT is non-covalent functionalization, i.e., formation of CNT complexes with organic molecules through non-covalent bonds (van der Waals or π-π stacking interactions). Various polymers and biological macromolecules such as peptides and nucleic acids act as organic molecules (Andrews et al. 2002). An advantage of this method is that the electronic structure of the CNT surface is preserved (Priluts'ka et al. 2009).

Covalent functionalization of CNT involves covalent attachment of molecules, e.g., peptides, organic acids, polyamines, and poly-L-lysine, to CNT walls in order to improve their solubility (Fig. 3.1). It was achieved via 1,3-dipolar cycloaddition, amination, or esterification of COOH groups after CNT are purified of side products (amorphous C and the metal particles used to grow the CNT (Priluts'ka et al. 2009).

An important advantage of both covalent and non-covalent functionalization is that more stable colloidal dispersions based on these CNTs can be prepared and new nanomaterials can be formed from them.

Besides that, poly-ionic liquid (PIL) is an important modifier of NM PCM. Thus, the preparation of a gel for ionic liquids with CNT has allowed to expand the spectrum of the use of ionic liquids as modifiers for CNT (Takanori Fukushima and Takuzo Aida 2007). For example, upon being grounded into ionic liquids, CNT bundles are untangled. And the resultant fine bundles form a network structure of CNT. This is due to the possible specific interaction between the imidazolium ion component and the π-electronic CNT surface. As a result, the received gelatinous materials, consisting of highly electroconductive nanowires and fluid electrolytes, can be utilized in a wide variety of electrochemical applications. Among them one can single out sensors, capacitors, and different kinds of actuators. Besides that, the poly-ionic liquids allow for non-covalent and covalent modifications of CNTs and fabrication of PCM with enhanced physico-mechanical properties. The processing of CNTs with PIL is not accompanied by the disruption of the π-conjugated CNT structure and does not require solvents. Therefore, it can readily be scaled up.

3.3.3 Preparation of Carbon Nanomaterial Dispersions in Organic Solvents and Rubber

Recently, carbon materials have been investigated mainly using low-frequency US treatment of the reaction mixture. This enhances disintegration of carbon material aggregates and forms surface defects on them (Luzgarev et al. 2013). This increases the chemical reactivity of the CNM surface (Luzgarev and Denisov 2005). As a rule, US baths, immersed and flow US dispersers, and high-speed mechanical dispersers (simultaneously with US devices) are used for low-frequency US treatment. However, the poor mechanical characteristics of the starting NMPCM limit their scope of application (Badamshina et al. 2010).

The possibility of producing stable dispersions of carbon materials in organic solvents and high-molecular-mass polydimethylsiloxane rubber SKT was studied (Luzgarev et al. 2013). The organic solvents toluene and benzene were used to prepare the dispersions. Optical microscopy found that the maximum particle sizes were small (30–40 μm) if an immersion US disperser (operating frequency 22 kHz) was used. Dispersion carried out in a US bath (operating frequency 25 kHz) formed large particles (80–100 μm). Carbon material of PUM grade could not be dispersed using this method.

A high-speed electromechanical disperser did not give high degrees of dispersion. The particle sizes of the carbon materials were 300–400 μm. Furthermore, dispersions prepared using US tended to aggregate rapidly (1.5–4 min) and form flakes that subsequently settled regardless of the carbon material concentration and used organic solvent. However, aggregated dispersions prepared using an immersed US disperser were easily restored by repeated treatment in a US bath.

3.4 Preparation and Study of Epoxide Nanocomposites

Recent research identified CNT as the most promising platform for designing materials with fundamentally new properties (Vorob'eva et al. 2011). CNTs differ from other nanofillers (ultrafine particles, organic clays) by the presence of an atomically smooth surface. This stretches matrix-polymer macromolecules on the surface and forms a densely packed polymeric-matrix-CNT interfacial layer.

An increased fracture strength ε_f of NMPCM filled with CNT compared with the starting matrix polymer or increased plasticity of nanocomposites (Vorob'eva et al. 2011), e.g., epoxypolymer-CNT nanocomposites (Khabashesku et al. 2007) and others, was reported several times. Increased plasticity for this class of NMPCM is rather general in nature.

This effect is very important from a practical viewpoint because the main deficiency of PCM is their brittleness. The ε_f value decreases as the filler content increases. Therefore, it is important to estimate theoretically the effect of increasing the plasticity of reactoplastic-polymer-CNT nanocomposites. This can produce NMPCM with a unique set of operational properties, i.e., a simultaneous increase of stiffness, strength, and plasticity. However, uneven filling of the polymer matrix by CNT increases the NMPCM brittleness. Individual nanotubes are broken at relatively low loadings (Wagner et al. 1998).

Low-frequency US treatment is one of the most effective methods for distributing CNT evenly in a polymer matrix. CNTs are effectively distributed in an acetone/EtOH mixture (9: 1) at ~50 °C for an US irradiation time of ~10 min (Brent et al. 2011). The following conclusions were drawn based on the experimental results (Tkachev and Zolotukhin 2007). Preliminary activation (in particular, US) of the polymer matrix in a mixture of organic solvents is required to create CNT-modified composites. The optimum CNT concentration in the composite (determined experimentally) lies in a certain range, e.g., 0.4–0.8 wt.%. As a rule, increasing the CNT content above 1 mass% decreases considerably the strength of the final NMPCM. The operational characteristics of composites based on epoxide diane oligomer ED-20 could be increased considerably (by 1.5–2.0 times) by using CNT as the filler.

It was reported that a material was made that only became stronger at regular loads (Brent et al. 2011). The created nanocomposite consisted of a forest of vertical MWCNT, the gaps among which were filled with polydimethylsiloxane. Cyclic loading of this material did not generate mechanical fatigue, like for classical PCM, but strengthened the NMPCM. Compression of a sample at a frequency of five times per second for a week increased the sample stiffness by 12%.

3.4.1 Features of Nanocarbon Modification of Epoxide Oligomers

Effects of employed nanodisperse fillers on the physico-mechanical properties of the filled polymers must be analyzed during development of an actual NMPCM industrial process. The properties of the final PCM with nano-sized fillers (as compared with micro-sized fillers) are difficult to predict (Kolosov 2015b) because several factors related to adhesion and cohesion mechanisms and aspects of NMPCM destruction must be considered. A potential destruction mechanism of the disperse-filled polymer matrix that occurs most often in construction PCM was discussed before (Blokhin 2012). Disperse inclusions present an actual barrier to the advancing crack front in a stress-strained NMPCM. The crack propagation front lengthens as each pair of adjacent dispersed nanoparticles passes between them.

According to the Lang model, lengthening of the crack front can contribute considerably to the destruction energy of a brittle composite, e.g., one based on an

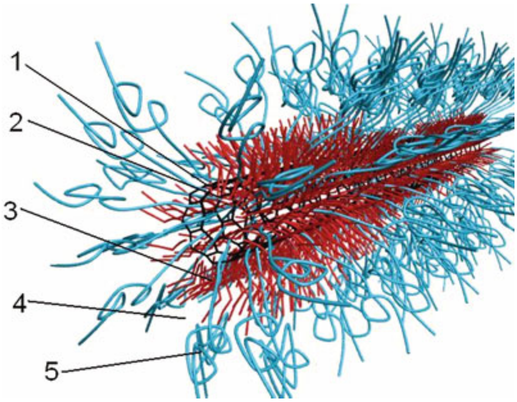


Fig. 3.2 Schematic of polymer-CNT boundary layer morphology (Blokhin 2012): (1) CNT, (2) adsorbed polymer microlayer, (3) oriented polymer layer, (4) polymer transition layer, (5) polymer in bulk phase. (Modified after Blokhin 2012)

EP (Blokhin 2012). The size of the disperse particles also affects crack propagation. Larger particles cause larger stressed zones (within a particle and around it), and therefore, more destructive deformation energy is accumulated due to the effect of the particle (Blokhin 2012). External stresses applied to the material should not exceed the strength limit (for brittle materials) or the flowability limit (for plastic materials). With this condition, the critical sizes of inclusions d_{cr} at which the material can stratify along matrix-filler interfaces can be estimated. The orienting effect of a disperse filler on the polymer binder is important. Shrinkage on the microscale level that is observed during NMPCM forming also causes spatial orientation (Fig. 3.2).

The formation in the NMPCM bulk of a three-dimensional framework of nanofiller particles alternating with a structured hardened polymer matrix is an important factor. The framework is formed by boundary layers of polymer matrix, whereas disperse filler particles are boundary layer carriers. The disperse filler must be evenly distributed in the NMPCM in order to form a continuous reinforcing three-dimensional framework of filler particles and structured reactoplastic polymer layers. Thus, the conditions for producing a positive effect upon filling the highly cross-linked thermoreactive polymer matrix with hard disperse particles are (1) optimal degree of filling (depends on disperse particle size), (2) particle sizes in the nanometer range, and (3) good adhesion of filler to polymer matrix, preferentially with the ability to form a chemical bond between the filler and matrix.

Research on the influences of the filling parameters and the nature of disperse particles on structural changes in the polymer taking into account features of the reactoplastic NMPC is crucial. Distribution processes of disperse particles in a liquid epoxide binder (EB), the influence of modifying the matrix with carbon nanoparticles, and the development of effective technologies for introducing nanoparticles into the liquid (EB or EO) must be investigated.

Experiments on the incorporation, distribution, and stabilization of a dispersion using MWCNT (Blokhin 2012) showed that physico-mechanical characteristics increased insignificantly for low percent MWCNT contents (from 0.01 wt.% to 1 wt.%). The absolute value decreased with increasing percent content of solid

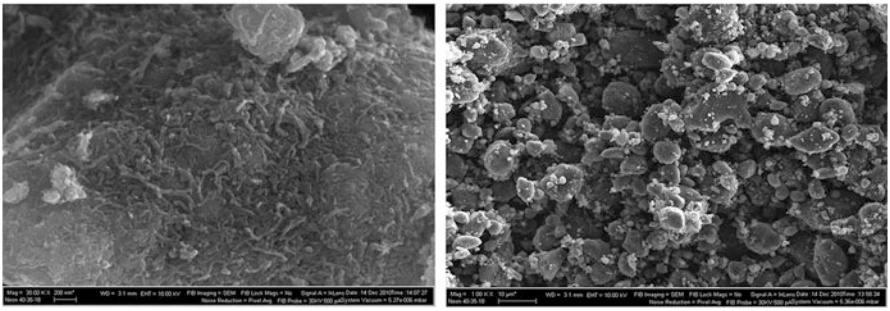


Fig. 3.3 SEM images of MWCNT after the best treatment, regime in a planetary mill; dispersion of agglomerated particles was observed to increase (Blokhin 2012)

phase in the dispersion. Simple (mechanical) mixing of CNT with EO was ineffective for improving the physico-mechanical characteristics. A large part of the suspension particles were agglomerates consisting of significantly shortened CNT. As a rule, their dimensions were out of the nanoscale range. However, air adsorbed on the surface and within agglomerates was entrained with them into the polymer matrix if they were added. Therefore, agglomerates had to be disintegrated and distributed evenly in the EB bulk for modification of EO with CNT.

Methods for disintegrating and distributing MWCNT in liquid EB were tested (Blokhin 2012). These included high-energy impact of milling balls and friction between balls and the wall of the milling vessel (in a ball mill): stretching, compressing, and shear forces, elevated temperatures, and static electricity (in a roll mill); and US irradiation. The equivalent particle sizes increased upon treatment in a planetary mill (Fig. 3.3) because of agglomeration and combination into globules. The optimum US irradiation time was ~6 min in a highly viscous medium (Blokhin 2012). The physico-mechanical characteristics of the hardened binder were worse by an order of magnitude if surfactant was added to the composition. Apparently, this was a consequence of blocking nanoparticle active sites. An MWCNT concentration of 0.5 wt.% gave the best physico-mechanical characteristics for functionalized MWCNT. However, the cost of functionalized MWCNT was significantly greater than that of the starting MWCNT.

The thermal conductivity of the epoxide NMPCM doubled if 10% MWCNT was added. Also, adding CNT meant that the final NMPCM would be electrically conductive because the electrically conductive CNT particles formed a closed three-dimensional framework in the EO during its polymerization. A nanomodified binder in fiberglass can increase by about eight times for the optimal regimes its resistance to bending stresses (the bending fracture load with fibers distributed along the sample increased from 1 kg to 11 kg; with fibers distributed transversely, from 1.4 kg to 8.0 kg) (*Blokhin* 2012). Incorporation of MWCNT into a liquid polymer matrix promotes the ability to control the formation of its structure. For example, the dimensions of pultrusion parts can be controlled to provide high throughput and the required quality level (*Blokhin* 2012).

The physico-mechanical characteristics (with respect to bending loads) improved after nanomodification of an EB by an average of 20–30% and the compression strength limit and heat resistance by 70%. The destructive load of fiberglass increased by 2–3 times (*Blokhin* 2012).

3.4.2 Roller Dispersion of Highly Viscous Suspensions of Epoxide Oligomers with CNT

Liquids can be dispersed using homogenizers; colloidal mills; injection mixers and nozzles (operating on the jet pump principle); turbine, propeller, and other types of high-speed stirrers; acoustic and electrical devices such as US whistles and horns; magnetostrictive transducers; and wave concentrators (spray nozzles) for generating aerosols (Rebinder 1979*;* Avakumov 1989). Two designs for roll dispersers (Abdrakhimov et al. 2012) that can control the dispersion processing parameters are based on the 80E disperser design of the German company EXAKT (calendar with shear zone between rolls) (www.exakt.de/Produkte.6.0.html), which is effectively used to produce nanosuspensions. The disperser (Fig. 3.4) comprises three parallel rolls (cylinders) of the same diameter (80 mm) that are arranged with controlled gaps of 10–500 μm and rotate at different rates ($\omega < 100$ rpm) pairwise in opposite directions with a ratio of rates of 9:3:1 in addition to combs for removing the finished product.

The main deficiency of the disperser (www.exakt.de/Produkte.6.0.html) is the insufficient degree of agglomerate destruction (Fig. 3.5). Therefore, the dispersion cycle had to be repeated several times.

MWCNT agglomerates are distributed and are soaked with EO, which replaces air bubbles in the starting agglomerate structure, as the filled liquid EO composite containing MWCNT passes through the gap between the rolls (through the action of shear flow in the gap between rolls). It must be considered that the composite viscosity increases as the filler concentration increases. This increase may not be proportional to the filler content in the liquid polymer medium. The composite undergoes preliminary degassing at the outlet of the roll mill. This has a positive

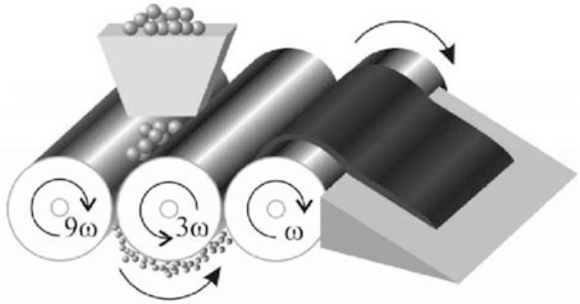
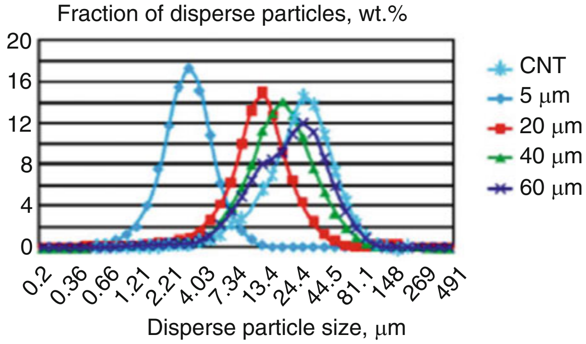


Fig. 3.4 EXAKT three-roll mill-disperser (www.exakt.de/Produkte.6.0.html)

Fig. 3.5 Typical MCNT particle-size distributions after processing in EXAKT three-roll mill with various gaps between the rollers (Blokhin 2012). (Modified after Blokhin 2012)



effect on the mechanical properties of the final product. The average experimental dispersion of MWCNT in EO after roll processing turned out to be equal to the gap between the rolls multiplied by 0.6 (Blokhin 2012).

According to the investigations in scientific literature, the resulting intertwined balls of CNT in EO can be dispersed by applying a shear stress of at least 1 MPa (duration not given) (Wichmann 2009). However, the scientific literature has practically no data on the agglomerate sizes, average lengths, and dimensions of single CNT in the agglomerate. Therefore, the dispersion time parameters are difficult to determine. Thus, the relationship of the disperser parameters for a given volume content of nanofiller φ and temperature T must be determined (analytically) in order to design an industrial process for dispersing CNT in a viscous polymer using roll systems. The parameters are the roll diameter D_r, rotation rate ω, gap between rolls δ, and dispersion time considering the average sizes and lengths of the added CNT.

Taunit-MD CNT, which consists of threadlike formations of polycrystalline graphite as a friable powder of black agglomerates, was used in the study (Abdrakhimov et al. 2012). The agglomerate structure (micrometer dimensions) contained intertwined bundles of MWCNT (http://nanotc.ru/index.php?option=com_content&task=view&id=8&Itemid=34). The CNT parameters were monitored using transmission electron microscopy. Single bundled CNT were 2–5 times shorter than straightened CNT (Fig. 3.6). The CNT outer diameter was 10–50 nm; inner diameter, 3–8 nm; and length, >2 μm.

A matrix produced from epoxide diane oligomer ED-20 and hardener methyl isotetrahydrophthalic anhydride (iso-MTHPA) had heat resistance temperature of 170 °C, which enabled nanocomposites prepared from it to be used at temperatures up to 120 °C. A roll disperser with a vertical rotor and stator was developed (Abdrakhimov et al. 2012). The stator was a thick-walled beaker with a removable cap (inner diameter 32 mm) situated on the lower end; the rotor, a cylinder 30 mm in diameter; the drive, an electric motor capable of rotating at 500–2500 rpm; and a moveable stage allowing the required gap δ to be set. The required gap for these dimensions was $\delta = 6.3$ μm. The stretching deformation for this was $\varepsilon_s = 33$, which was sufficient to destroy the agglomerates.

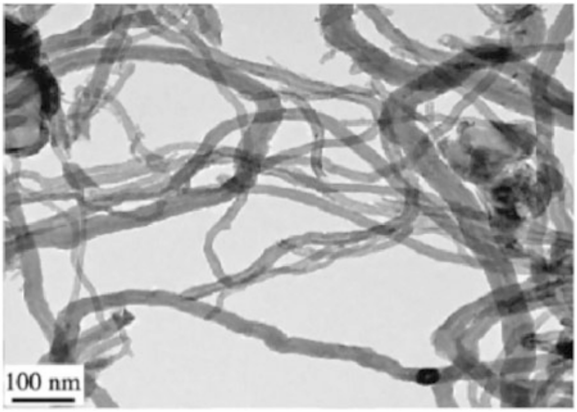


Fig. 3.6 Taunit-MD CNT in JEOL JEM 2100 transmission electron microscopy (×25,000) (Blokhin 2012). (Modified after Blokhin 2012)

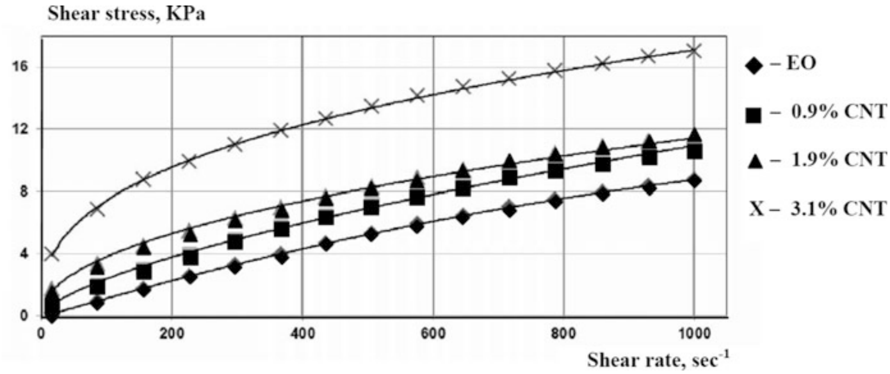


Fig. 3.7 Flow curves of EO-CNT composites (Blokhin 2012). (Modified after Blokhin 2012)

A mixture of CNT and oligomer was poured into the gap between the stator and rotor (Abdrakhimov et al. 2012). The mixture was drawn into the gap as the rotor rotated. Shear in the gap developed stresses up to 1 MPa, which were sufficient to destroy CNT agglomerates (Wichmann 2009). The suspension experienced self-heating during dispersion at high rotor rotation rates and small gaps. This also helped to decrease the viscosity of the oligomer and the shear stresses. Working parts of the disperser were periodically cooled in order to avoid overheating. The suspension viscosity was measured as a function of shear rate and CNT mass fraction on a cone-plane viscometer at shear rates 17–1000 s^{-1} and 27–100 °C (Fig. 3.7).

Figure 3.8 shows that rate of viscosity reduction increased as the mass fraction of CNT in the polymer matrix increased. So, the above results show the prospects of further research in this direction.

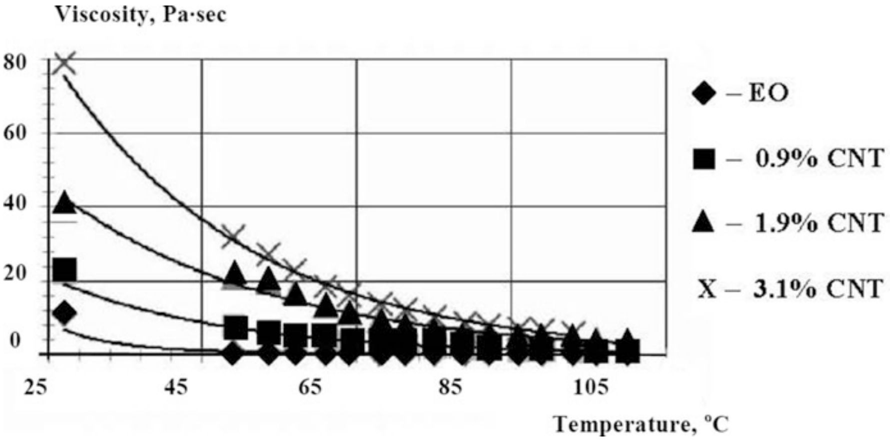


Fig. 3.8 Viscosity of EO-CNT composites as functions of temperature (Abdrakhimov et al. 2012). (Modified after Abdrakhimov et al. 2012)

3.4.3 Solidified Nanomodified Oligomers Microstructure

The choice of an effective method for introducing nanoparticles into a polymer matrix, ensuring an even distribution of the fibers in the polymer, and optimizing the operating regimes is important for preparing PCM with a reinforcing nanofibrous filler (Muranov et al. 2012).

CNTs aggregate in the matrix because of the high CNT surface energy. The aggregates can reach lens and hundreds of micrometers in size. In this instance, the matrix is not strengthened mechanically and reinforced (which is characteristic for uniformly distributed nanoparticles). The mechanical and physical properties of the NMPCM are degraded (Ray 2006; Smrutisikha 2010; Kolosov 2015b).

Nanomodified samples of a solidified oligomer containing a finely dispersed fiberglass filler and modified CNT of various contents (0%, 5%, 30%), a polymer matrix of cold-hardened polyester oligomer, and CNT (Baylubes® C 150 P, agglomerates of several CNTs with small outer diameters, narrow diameter distribution, and ultrahigh side ratio) were investigated before (Muranov et al. 2012).

Samples were analyzed by scanning electron microscopy with preliminary deposition of a gold conducting layer in order to eliminate accumulation of static charge on the surface of the dielectric material (Fig. 3.9).

Elemental analysis of NMPCM samples by energy-dispersive microanalysis showed that the studied section of the microfiller had the following distribution of element concentrations (at %): C, 28; Si, 21; O, 25; and Au, 26. CNTs were distributed in the polymer matrix noticeably more uniformly for a CNT content of 5% than for 30%.

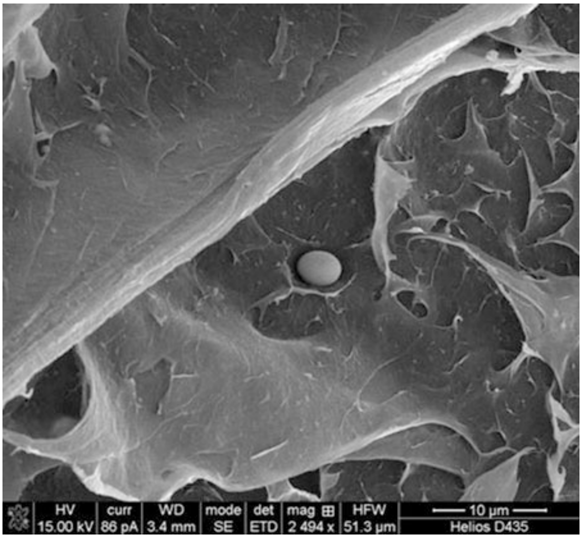


Fig. 3.9 SEM image of NMPCM surface with deposited gold film (Muranov et al. 2012)

3.5 Use of Carbon Nanotubes to Improve the Physico-mechanical and Operational Characteristics of Polymers

The existing structure of CNT makes it possible to create on its basis PCM with improved physico-mechanical and operational characteristics. These include static strength, fatigue strength, electrical conductivity, an extended range of operating temperatures, and some special properties of NM PCM. In connection with this, intensive studies of new properties are being carried out, which are obtained with a small addition of multi-walled CNT to polymers, for example, fire resistance and anti-putrefaction and a number of others.

The above combination of properties and form of the product, compatible with modern technologies for the processing of classical polymers, will result in the synthesis of new structural materials that can be used in a wide range of applications. The results of these studies may lead to the development of new products more in line with modern environmental requirements and improved performance compared to existing materials.

The use of CNT for commercial purposes is a reality today, which attracts increasing attention. This means that they are accepted by industry as a component of added value, competing with other options that are governed by industry standards. At present, new useful and unpredictable properties of CNT are being investigated, which will allow them to expand their penetration into the polymer industry. But the creation of such materials is a complex task, which requires a large number of experimental studies.

In this section we briefly discussed the questions concerning with use of CNT to increase the strength and heat resistance of EB, fatigue characteristics of NMPCM, and electrical conductivity of PCM modified by CNT.

3.5.1 Use of Carbon Nanotubes to Increase the Strength and Heat Resistance of Epoxide Binders

A critical problem in mechanical engineering is the development of heat-resistant binders for PCM intended for construction (Kondrashov et al. 2013). The traditional approaches for solving this problem (creation of polymeric reactoplastic binders with the maximum possible network of chemical cross-links) are not always effective.

The tensile strength of PCM is determined by the balance between the number of chemical cross-links that increase the elasticity modulus and glass-transition temperature T_g and the number of physical sites for network cross-linking that provide a uniform redistribution of stresses between the chemical network sites as a result of relaxation processes.

Therefore, the tensile strength at first increases with an identical number of physical network sites and increased number of chemical cross-links. It then decreases when the number of chemical cross-links becomes sufficiently dense to freeze relaxation processes (Kondrashov et al. 2013).

One possible solution to this problem is to modify the epoxy resin with functionalized CNT, in particular, CNT with surfaces functionalized by amines (Kondrashov et al. 2013). The CNT diameter before fictionalization by non-covalently bonded amines was 20 nm; after, 40 nm. The glass-transition temperature T_g of an epoxy nanocomposite containing *0.5%* functionalized CNT was 41 °C greater than that of the starting composite if the developed method was used for modification. The increasing in glass-transition temperature was associated with an increase of the elasticity modulus E for tensile strength σ_t (Table 3.1).

An analysis of the stress-elongation diagram showed that the strength improved due to an insignificant (8%) increase of the elasticity modulus and a considerable (25%) increase of the fracture strength 8% of the studied nanocomposites. Thus, CNT functionalized with various groups can be used to increase the healing resistance of construction EB and also to soften heat-resistant binders with low fracture strength. Use of functionalized CNT as modifiers for heat-resistant EB is a promising research direction.

Table 3.1 Physico-mechanical and operational properties of EC modified by functionalized CNTs (Kondrashov et al. 2013)

Composite composition	T_g (°C)	E (GPa)	σ_t (MPa)	$\varepsilon_{f,}$ (%)
ER – diglycidyl ether of bisphenol F				
Starting composite 1	170.15	2.0	72.6	5.4
Modification by 0.3% CNT	164.64	23	713	4.6
Modification by 0.3% ACNT[a]	158.86	23	88.5	7.5
ER – diglycidyl ether of bisphenol A				
Starting composite 2	–	3.29	63.8	735
Modification by 0.1% CNT	–	3.35	623	125
Modification by 0.1% ACNT[a]	–	33	69	7.7

[a] CNT functionalized by amines (composite 1, toluenediamine; composite 2, polyamine)

T_g glass-transition temperature, E elasticity modulus, σ_t tensile strength, ε_f fracture deformation

Table 3.2 Strength characteristics of the composite (Shestakov et al. 2012)

Samples	σ_t (MPa)	ε_f (%)	σ_{02} (MPa)	ε_{02} (%)	E (MPa)
Without CNT	76,8	7	60	1,2	5000
With CNT, without functional groups	87,0	6	60	1,2	5000
With CNT + functional groups	110,0	7	80	1,4	5714

σ_t tensile strength, ε_f fracture deformation, σ_{02} yield stress, ε_{02} yield strain (flowing deformation), E elasticity modulus

3.5.2 Fatigue Characteristics of Polymer Nanocomposite Materials

Numerous experiments show that the incorporation of CNT with grafted functional groups into the liquid matrix of the PCM significantly improves the strength and fatigue characteristics of the solidified reactoplastic PCM. For example, the studied composite was an epoxide oligomer ED-20 reinforced with fiberglass (Shestakov et al. 2012). Before the reinforcement, the CNT was incorporated into the ED-20. Its amount was 0.1% of the polymer matrix weight. In one case, the CNTs were incorporated without functional groups and in the other with functional groups grafted on the outer surface of a CNT. Thus, with the incorporation of CNT, the structure of the material was changed. The experiments were performed on static deformation and fatigue life of standard flat-solidified EC samples. The composition of the samples is presented in Table 3.2, and the results of the fatigue strength experiments are shown in Fig. 3.10.

The results of the experiments indicate that the tensile strength σ_t in the samples with CNT without functional groups increased by 13%, and the fracture deformation ε_{f} corresponding to the tensile strength σ_t decreased by 14%. At the same time, the

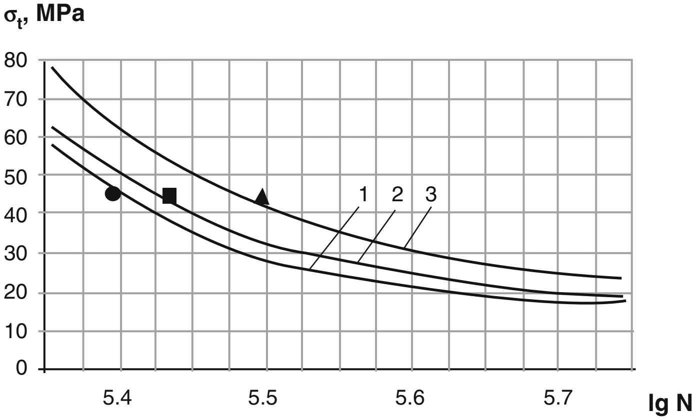


Fig. 3.10 Fatigue destruction curves of polymer composites: (1) without CNT, (2) modification with pure CNT, (3) modification with CNT and with grafted functional groups; N, number of loading cycles. (Modified after Shestakov et al. 2012)

yield stress σ_{02}, the flowing deformation ε_{02} corresponding to the yield stress σ_{02}, and the elasticity modulus E have not changed. The restricted limit of fatigue durability on the basis of $N = 500{,}000$ loading cycles has not changed. Incorporation of CNT with grafted functional groups in a liquid epoxy matrix showed better results than in the previous case. The breaking point σ_t of such samples increased by 43%, and the fracture deformation, ε_f, corresponding to the tensile strength, σ_t, did not change.

In turn, the yield stress σ_{02} of nanocomposites based on CNTs with grafted functional groups increased by 33%, the deformation ε_{02} corresponding to the yield stress σ_{02} increased by 16%, and the absolute value of elasticity modulus E increased by 14%. The restricted limit of fatigue durability on the basis of $N = 500{,}000$ cycles of loading increased by 20%.

Thus, the conducted experiments have shown that the incorporation of CNTs with grafted functional groups significantly improves the strength and fatigue characteristics of NMPCM.

3.5.3 *Electrical Conductivity of Polymer Composite Materials Modified by Carbon Nanotubes*

A promising direction of polymeric material science is the creation of PCM that have the necessary functional properties (the so-called "functional" PCM). One such important property is the electrical conductivity of PCM, which is carried out by modification with CNT. It was found that the conductivity of nanocomposites with CNT is influenced not only by the type, the concentration of CNT, and the composition of the polymer matrix but also by the technologies for obtaining a nanocomposite. For example, the use of extruders that provide a high level of shear stresses makes it possible to obtain hybrid PCM, which simultaneously combine high electrical conductivity and high physical and mechanical properties.

It is shown that the use of carbon nanotubes as the main reinforcing filler makes it possible to obtain PCM with a record tensile strength of 3.8 GPa, an elasticity modulus of 293 GPa, and a conductivity of 1230 Sm/cm. (Kondrashov et al. 2016). It was considered the possibility of giving functional properties to hybrid PCM, in which carbon nanotubes are used along with the basic reinforcing carbon fiber. The authors have used CNT dispersed in an EC with a three-roll mixer to make a hybrid PCM (Reia da Costa et al. 2012). For the manufacture of PCM, the transfer molding method was used.

The analysis showed that the use of such technology for the production of carbon plastics makes it possible to increase the electrical conductivity in a direction perpendicular to the laying plane by a factor of 2 compared to the initial one – up to 200 Sm/cm. In the case of glass-reinforced plastic, the electrical conductivity increases from $7 \cdot 10^{-8}$ Sm/cm to $5 \cdot 10^{-7}$ Sm/cm. At a distance of 30 cm from the inlet, the electrical conductivity decreased by 50%. The obtained results show that this method is unpromising for giving the PCM functional properties (Reia da Costa et al. 2012).

Another approach to this problem was demonstrated by the group of authors (Garcia et al. 2008). According to this investigation, CNTs were grown on alumina fabrics by chemical vapor deposition (CVD), which was then impregnated with an EC, followed by compression at room temperature for 12 h and final curing at 60 °C. The electrical conductivity of the obtained PCM was 3–5 Sm/cm in the laying plane and 3–4 Sm/cm in the perpendicular direction at a concentration of CNT: 1–3% (by weight). The authors also noted an increase in the tensile strength at the interlayer shear τ_s in the hybrid PCM (33.8 ± 1.1 MPa) as compared to the control sample (20.1 ± 0.9 MPa) (Garcia et al. 2008).

A similar approach has been applied by the authors in the work for PCM based on carbon fibers with the additional use of carbon fiber felt as a substrate for the growth of CNT (Singh et al. 2014). After impregnation of the felt with the EC by hot pressing, a PCM with a high content of CNT was obtained – up to 18% (by weight). Investigations of mechanical properties showed that the value of the bending strength increased from 85 MPa to 115 MPa. The electrical conductivity increased from 3 Sm/cm to 18 Sm/cm. At the same time, this approach requires careful selection of CVD process parameters, since using this method of growing CNT on the surface of glass and carbon fibers leads to a drop in their tensile strength (Lubineau and Rahaman 2012).

In conclusion, we note that to simulate the process of introducing sensors designed to monitor the state of NMPCM, including so-called intelligent (smart) PCM based on them, different types of sensors are currently used (Hu et al. 2010). Modeling the electrostatic control over depth of the introduction of intelligent sensors into a polymer composite material is studied in Ivitskiy et al. (2017). Simulation of nanomodified polymers testing by the electric capacitive method is investigated in a study by Bazhenov et al. (2017). Aspects of automation of intelligent sensor injection inlet in polymer moldings by using vector controlled electric drive are investigated in a study by Sivetskyy et al. (2017). In this case, the introduced sensors, depending on their size, can be considered as a kind of micro- or even nanomodifier of PCM. In conclusion, we note that to simulate the process of introducing sensors designed to monitor the state of NMPCM, including so-called intelligent (smart) PCM based on them, different types of sensors are currently used (Hu et al. 2010).

3.6 Conclusions

The study results described in this chapter confirm the effectiveness of physical, chemical, and combined physicochemical modification methods as a basic direction for improving the technological and operational characteristics of classical and NM liquid polymer media and reinforced PCM on their basis. The technology for NMPCM production depends on the type of particle nanomodifiers that are incorporated into the liquid polymer system. The high surface energy of nanoparticles creates certain difficulties for combining them with a liquid polymer matrix. It leads to adhesion and aggregation of particles, that is, formation of fullerites.

Agglomerating of excess of CNT leads to a sharp decrease in the strength of polymerized samples. Thus, we can consider CNT agglomerates as a kind of tension concentrators. Operating properties of produced NMPCM can be highly scattered if the dispersion quality is insufficient. Therefore, nanoparticles should be added first to the least viscous binder component (low-viscosity hardener).

Incorporated nanoparticles are very active; they enter into a chemical reaction with other substances quickly and lose their unique properties. Therefore, it is difficult to obtain NMPCM using traditional methods for composites. Various solutions and surfactants are used for dispersing fillers, including methods using US cavitation action. Therefore, US treatment, as the most effective method which is used in the stages of de-agglomeration, dispersion of nanoparticles in liquid polymer media, and also further combination of components of classical and NMPCM, deserves special attention.

Functionalized with different functional groups, nanomodifiers in the form of CNT are used to increase the heat resistance of EB used for structural purposes, as well as for the elasticization of heat-resistant binders characterized by small tensile deformation. In this case, the use of functional CNTs as modifiers of heat-resistant EB is a promising direction for future research. The optimal concentration and uniform distribution of CNT in the polymer binder play a decisive role in the final hardening of NMPCM.

The analyzed research results for nanocarbon-modified EO and the approaches used to solve actual problems could be applied to studies of new types of NMPCM. In general, the effects of filling parameters and the nature of the disperse particles on structural changes in the polymer, considering features of reactoplastic polymeric binders and nanodisperse fillers, must be investigated.

References

Abdrakhimov RR, Sapozhnikov SB, Sinitsir VV (2012) Analysis of suspension rheology for effective dispersion of MWCNT in epoxy resin. Vestn Yuzhno-Ural Gos Univ Ser Mat Mekh Fiz 34:68–74

Aldoshin SM (2008) Polymer nanocomposites – a new generation of polymeric materials with improved operational characteristics. In: Proceedings of International forum on nanotechnologies, vol 1. Rusnanotech 08, Rosnano, Moscow, pp 385–386

Andrews R, Jacques D, Qian D, Rantell T (2002) Multiwall carbon nanotubes: synthesis and application. Acc Chem Res 35:1008–1017

Atovmyan EG, Badamshina ER, Gafurova MP et al (2005) Synthesis of new polyhydroxylated fullerenes. Dokl Akad Nauk 402(2):201–203

Avakumov EG (1989) Mechanical methods for activating chemical processes. Nauka, Novosibirsk

Badamshina ER, Gafurova MP (2008) Modification of polymer properties by doping with fullerene C_{60} (review). Vysokomol Soed Ser A 50(8):1572–1584

Badamshina ER, Gafurova MP, Estrin Ya I (2010) Modified carbon nanotubes and synthesis of polymer composites with them. Usp Khim 79(11):1027–1064

Bazhenov V, Protasov A, Ivitskiy I, Ivitska D (2017) Simulation of nanomodified polymers testing by the electric capacitive method. Eastern-European Journal of Enterprise Technologies 4 (5 (88)):4–9. https://doi.org/10.15587/1729-4061.2017.108460

Blokhin AN (2012) Process development and apparatus for nanocarbon modified composites of epoxide resins. PhD thesis, Tambov

Brent CJ, Patra KP, Ci L et al (2011) Observation of dynamic strain hardening in polymer nanocomposites. ACS Nano 5(4):2715–2722

Coleman JN, Khan U, Blau WJ, Gun'ko YK (2006) Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites. Carbon 44(9):1624–1652

Fukushima T, Aida T (2007) Ionic liquids for soft functional materials with carbon nanotubes. Chem Eur J 13:5048–5058. https://doi.org/10.1002/chem.200700554

Garcia EJ, Wardle BL, Hart AJ, Yamamoto N (2008) Fabrication and multifunctional properties of a hybrid laminate with aligned carbon nanotubes grown in situ. Compos Sci Technol 68:2034–2041

Harris PJF (2004) Carbon nanotube composites. Int Mater Rev 49(1):31–43

Hirsch (2002) Functionalization of single-walled carbon nanotubes. Angew Chem Int Ed 41 (11):1853–1859. http://nanotc.ru/index.php?option=com_content&task=view&id=8&Itemid=34

Hu N, Karube Y, Arai M et al (2010) Investigation on sensitivity of a polymer/carbon nanotube composite strain sensor. Carbon 48:680–687

Ivitskiy I, Sivetskiy V, Bazhenov V, Ivitska D (2017) Modeling the electrostatic control over depth of the introduction of intelligent sensors into a polymer composite material. Eastern-European Journal of Enterprise Technologies 1(5(85)):4–9. https://doi.org/10.15587/1729-4061.2017.91659

Karimov AA, Kolosov AE, Khozin VG, Klyavlin VV (1989) Impregnation of fibrous fillers with polymer binders. 4. Effect of the parameters of ultrasound treatment on the strength characteristics of epoxy binders. Mechanics of composite materials 25(1):82–88. https://doi.org/10.1007/BF00608456

Karpacheva GP (2000) Fullerene-containing polymers (review). Vysokomol Soed Ser C 42 (11):1974–1999

Khabashesku VN, Barrera EV, Lobo RFM (2007) Confined tubular carbon nanostructures for nanoreactors and synthons. Curr Res Nanotechnol 1(2):165–182

Kolosov AE (1988) Impregnation of fibrous fillers with polymer binders. 1. Kinetic equations of longitudinal and transverse impregnation. Mechanics of Composite Materials 23(5):625–633. https://doi.org/10.1007/BF00605688

Kolosov AE (2014a) Prerequisites for using ultrasonic treatment for intensifying production of polymer composite materials. Chem Pet Eng 50(1–2):11–17. https://doi.org/10.1007/s10556-014-9846-5

Kolosov AE (2014b) Low-frequency ultrasonic treatment as an effective method for modifying liquid reactoplastic media. Chem Pet Eng 50(1–2):79–83. https://doi.org/10.1007/s10556-014-9859-0

Kolosov AE (2014c) Effect of low-frequency ultrasonic treatment regimes on reactoplastic polymer composite material operating properties. Chem Pet Eng 50(3–4):150–155. https://doi.org/10.1007/s10556-014-9871-4

Kolosov AE (2014d) Efficiency of liquid reactoplastic composite heterofrequency ultrasonic treatment. Chem Pet Eng 50(3–4):268–272. https://doi.org/10.1007/s10556-014-9893-y

Kolosov AE (2014e) Low-frequency ultrasonic treatment of liquid reactoplastic media with pressure variation. Chem Pet Eng 50(5–6):339–342. https://doi.org/10.1007/s10556-014-9904-z

Kolosov AE (2015a) Preparation of nano-modified reactoplast polymer composites. Part 1. Features of used nanotechnologies and potential application areas of nanocomposites (a review). Chem Pet Eng 51(7–8):569–573. https://doi.org/10.1007/s10556-015-0088-y

Kolosov AE (2015b) Production of high-quality traditional and nanomodifications of thermosetting plastic polymer composite materials. VPI VPK Politekhnika, Kiev

Kolosov AE (2016a) Preparation of reactoplastic nanomodified polymer composites. Part 2. Analysis of means of forming nanocomposites (patent review). Chem Pet Eng 51(9–10):640–645. https://doi.org/10.1007/s10556-016-0100-1

Kolosov AE (2016b) Preparation of reactoplastic nanomodified polymer composites. Part 3. Methods for dispersing carbon nanotubes in organic solvents and liquid polymeric media (review). Chem Pet Eng 52(1–2):71–76. https://doi.org/10.1007/s10556-016-0151-3

Kolosov AE (2016c) Preparation of reactoplastic nanomodified polymer composites. Part 4. Effectiveness of modifying epoxide oligomers with carbon nanotubes (review). Chem Pet Eng 52 (7–8):573–577. https://doi.org/10.1007/s10556-016-0235-0

Kolosov AE (2017) Preparation of reactoplastic nano-modified polymer composites. Part 5. Advantages of using nano-modified structural carbon-fiber composites (a review). Chem Pet Eng 52 (9–10):721–725. https://doi.org/10.1007/s10556-017-0259-0

Kolosov AE, Repelis IA (1989) Saturation of fibrous fillers with polymer binders 5. Optimization of parameters of the winding conditions. Mech Compos Mater 25(3):407–415. https://doi.org/10.1007/BF00614811

Kolosov AE, Repelis IA, Khozin VG, Klyavlin VV (1988) Impregnation of fibrous fillers with polymer binders. 2. Effect of the impregnation regimes on the strength of the impregnated fillers. Mech Compos Mater 24(3):373–380. https://doi.org/10.1007/BF00606611

Kolosov AE, Karimov AA, Khozin VG, Klyavlin VV (1989) Impregnation of fibrous fillers with polymer binders. 3. Ultrasonic intensification of impregnation. Mechanics of Composite Materials 24(4):494–502. https://doi.org/10.1007/BF00608132

Kolosov AE, Karimov AA, Repelis IA, Khozin VG, Klyavlin VV (1990) Impregnation of fibrous fillers with polymeric binders 6. Effect of parameters of ultrasound treatment on strength properties of wound fibrous composites. Mech Compos Mater 25(4):548–555. https://doi.org/10.1007/BF00610711

Kolosov AE, Sakharov OS, Sivetskii VI, Sidorov DE, Pristailov SO (2011a) Effective hardware for connection and repair of polyethylene pipelines using ultrasonic modification and heat shrinkage. Part 1. Aspects of connection and restoration of polymeric pipelines for gas transport. Chem Pet Eng 47:204–209. https://doi.org/10.1007/s10556-011-9447-5

Kolosov AE, Sakharov OS, Sivetskii VI, Sidorov DE, Pristailov SO (2011b) Effective hardware for connection and repair of polyethylene pipelines using ultrasonic modification and heat shrinkage. Part 2. Production bases for molding of epoxy repair couplings with shape memory. Chem Pet Eng 47:210. https://doi.org/10.1007/s10556-011-9448-4

Kolosov AE, Sakharov OS, Sivetskii VI, Sidorov DE, Pristailov SO (2011c) Effective hardware for connection and repair of polyethylene pipelines using ultrasonic modification and heat shrinkage. Part 3. Analysis of surface-treatment methods for polyethylene pipes connected by banding. Chem Pet Eng 47:216. https://doi.org/10.1007/s10556-011-9449-3

Kolosov AE, Sakharov OS, Sivetskii VI, Sidorov DE, Pristailov SO (2011d) Effective hardware for connection and repair of polyethylene pipelines using ultrasonic modification and heat shrinkage. Part 4. Characteristics of practical implementation of production bases developed using epoxy-glue compositions and banding. Chem Pet Eng 47:280. https://doi.org/10.1007/s10556-011-9460-8

Kolosov AE, Sakharov OS, Sivetskii VI, Sidorov DE, Pristailov SO (2011e) Effective hardware for connection and repair of polyethylene pipelines using ultrasound modification and heat shrinking. Part 5. Aspects of thermistor couplings and components used in gas-pipeline repair. Chem Pet Eng 47:285. https://doi.org/10.1007/s10556-011-9461-7

Kolosov AE, Sakharov AS, Sivetskii VI, Sidorov DE, Sokolskii AL (2012a) Substantiation of the efficiency of using ultrasonic modification as a basis of a production cycle for preparing reinforced objects of epoxy polymer composition. Chem Pet Eng 48(5–6):391–397. https://doi.org/10.1007/s10556-012-9629-9

Kolosov AE, Sakharov AS, Sivetskii VI, Sidorov DE, Sokolskii AL (2012b) Method of selecting efficient design and operating parameters for equipment used for the ultrasonic modification of liquid-polymer composites and fibrous fillers. Chem Pet Eng 48(7–8):459–466. https://doi.org/10.1007/s10556-012-9640-1

Kolosov AE, Sivetskii VI, Kolosova EP, Lugovskaya EA (2013) Procedure for analysis of ultrasonic cavitator with radiative plate. Chem Pet Eng 48(11–12):662–672. https://doi.org/10.1007/s10556-013-9677-9

Kolosov A. E., Virchenko G.A., Kolosova E.P., Virchenko G. I. (2015) Structural and technological design of ways for preparing reactoplastic composite fiber materials based on structural parametric modeling. Chem Pet Eng. Vol. 51, 7–8, pp 493–500. doi: https://doi.org/10.1007/s10556-015-0075-3

Kondrashov SV, D'yachkova TP, Bogatov VA et al (2013) Use of carbon nanotubes to increase the heat resistance of epoxide binders. Perspekt Mater 2:17

Kondrashov SV, Shashkeev KA, Popkov OV, Solovyanchik LV (2016) Perspective technologies for obtaining of functional materials of structural purpose on the basis of nanocomposites with CNTs (review). Electr Sci J "Proceedings of VIAM" 3(39):54–64

Lubineau G, Rahaman A (2012) A review of strategies for improving the degradation properties of laminated continuous-fiber/epoxy composites with carbon-based nanoreinforcements. Carbon 50:2377–2395

Luzgarev SV, Denisov VY (2005) Effective approach to modification of polysiloxane structure and properties. Sovr Naukoem Tekhnol 8:34–35

Luzgarev S., Tkachenko T.B., Moroz A.A., and Luzgarev S. V. (2013) Preparation of carbon material dispersions in polydimethylsiloxane rubber solutions. VestnKemGU Ser Khim 3 (55), pp 88–90

Muranov AN, Aleksandrov IA, Buyanov IA et al (2012) Microstructure of nanomodified polymer composites. Nauka Obraz 7:41–50. http://engineering-science.ru/doc/431361.html

Priluts'ka SV, Remenyak OV, Goncharenko YV, Prilutsky Y (2009) Carbon nanotubes as a new class of materials for nanobioengineering. Biotekhnologiya 2(2):54–66

Prylutska SV, Grynyuk II, Matyshevska OP et al (2008) Estimation of multiwalled carbon nanotubes toxicity in vitro. Phys E 40(7):2565–2569

Ray SS (2006) Polymer nanocomposites and their applications. American Scientific Publishers, Stevenson Ranch, pp 68–187

Rebinder PA (1979) Surface ejfects in disperse systems. Physicochemical Mechanics. Selected Works, Nauka, Moscow

Reia da Costa E.F., Skordos A.A., Partridge I.K., Rezai A. (2012) RTM processing and electrical performance of carbon nanotube modified epoxy/fiber composites. Compos A Appl Sci Manuf, 43, 4, pp 593–602

Shestakov PD, Galtsev AV, Tarasov AS (2012) Strengthening of polymer composites by carbon nanotubes. Int Sci Res J 11. https://doi.org/10.18454/IRJ.2227-6017

Singh BP, Bharadwaj P, Choudhary V, Mathur RB (2014) Enhanced microwave shielding and mechanical properties of multiwall carbon nanotubes anchored carbon fiber felt reinforced epoxy multiscale composites. Appl Nanosci 4(4):421–428

Sivetskyy VI, Khalimovskyy OM, Sokolskyy OL, Ivitskyy II (2017) Automation of intelligent sensor injection inlet in polymer moldings by using vector controlled electric drive. In: Proceedings of the IEEE 1st Ukraine conference on electrical and computer engineering (UKRCON '17); 29 May-2 June 2017; Kiev. IEEE; 2006. pp 534–537. https://doi.org/10.1109/UKRCON.2017.8100297

Smart SK, Cassady AI, Lu GQ, Martin DJ (2006) The biocompatibility of carbon nanotubes. Carbon 44:1034–1047

Smrutisikha B (2010) Dispersion and reinforcing mechanism of carbon nanotubes in epoxy nanocomposites. Bull Mater Sci 33(1):27–31

Tkachev G, Zolotukhin IV (2007) Apparatus and methods for synthesizing solid-state nanostructures. Mashinostroenie-1, Moscow

Vorob'eva EA, Bachurin KE, Makunin AV, Chechenin NG (2011) Synthesis and investigation of nanocomposites incorporating carbon nanotubes. In: Proceedings of 12th inter-institution school for young specialists concentration flows of energy in space electronics, ecology, and medical technology, Nov. 21–22, 2011, MGU, Moscow, pp 127–133

Wagner HD et al (1998) Stress-induced fragmentation of multiwall carbon nanotubes in a polymer matrix. Appl Phys Lett 72:188

Wang C, Guo Z-X, Fu S et al (2004) Polymers containing fullerene or carbon nanotube structures (review). Prog Polym Sci 29:1079–1141

Wichmann M (2009) Electrically conductive polymer Nanocomposite matrix system with load and health monitoring capabilities: Doct.-Eng. Dissert., Hamburg www.exakt.de/Produkte.6.0.html, http://nanotc.ru/index.php?option=com_content&task=view&id=8&Itemid=34

Chapter 4
Understanding Interactions of Nanomaterials with Soil: Issues and Challenges Ahead

Tropita Piplai, Tanushree Parsai, Arun Kumar, and Babu J. Alappat

Contents

4.1 Introduction 118
4.2 Methodology 122
4.3 Fate and Transport of Nanoparticles in Column Studies 124
4.4 Factors Affecting the Fate and Transport of Nanoparticles in Column Studies 127
  4.4.1 Water Characteristics 127
  4.4.2 Nanoparticle Characteristics 130
4.5 Conclusion 135
References 136

Abstract Nanotechnology is considered as a new generation of technology, which might have a revolutionary impact on economies through new consumer products, manufacturing methods, and material usage. Increasing studies showed the toxicity of different metal-based nanoparticles, which raises concerns over their fate and transport in the environment. The aim of this study was to improve understanding on the long-term interactions of nanomaterial with natural and undisturbed soil during land application of nanomaterial-contaminated sludge, to identify factors which affect their transport and mobility and identify issues and challenges.

Scientific databases were reviewed and different combinations of keywords were used. The major finding of this study included the effects of various properties, like pH, ionic strength, natural organic matter content, surface coating, size and aggregation of nanoparticles, sand/soil characteristics, and column flow characteristics on

---

T. Piplai · T. Parsai
Graduate Student, Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India

A. Kumar (✉)
Associate Professor, Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India
e-mail: arunku@civil.iitd.ac.in

B. J. Alappat
Professor, Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_4

the fate and transport of nanomaterials. These included variability in particle size and concentration, water chemistry (i.e., electrolyte species, ionic strength, and pH), flow velocity, and choice of collector surface. These findings were expected to improve fundamental understanding on fate and transport of nanomaterials in porous medium. It aimed to provide information on extents of retention of nanomaterials and associated ions in porous medium and the factors that regulate the deposition of these nanoparticles. It also intended to understand the effect of the presence of nanomaterials on the fate of ions associated with other nanomaterials and its implications. All these data were necessary to comprehend the long-term release and interaction dynamics of nanomaterials in the soil along with their chemical modification and transformation predicting their fate and transport in the soil media.

Keywords Nanomaterials · Fate · Transport · Porous medium · Surface chemistry · Ionic strength · Mixture · Natural organic matter

Abbreviations

APU	Amphiphilic polyurethane nanoparticles
CuO NPs	Copper oxide nanoparticles
DLVO	Derjaguin, Landau, Verwey, and Overbeek
NOM	Natural organic matter
nZVI	Nano-zerovalent iron
OECD	Organisation for Economic Co-operation and Development
TiO_2	Titanium dioxide nanoparticles
ZnO NPs	Zinc oxide nanoparticles

4.1 Introduction

Nanoparticle applications have been used in various agricultural, environmental, and industrial sectors of our society and might contaminate water, soil, and other environmental contaminants (Benn and Westerhoff 2008). In light of nanoparticles interacting with air, water, and soil, it is likely that it might impact human health in certain ways. Therefore, there are serious environmental and health issues related to these invisible, tiny particles because nanoparticles are very toxic and chemically active per unit of mass compared to the bulk materials of the same substances in a normal scenario. Therefore, treatment processes to eliminate and reduce nanoparticles in our waste treatment plants have to be explored in detail. Further, as domestic wastewater residuals are normally used as irrigation water and as soil-amendment materials, the chance of groundwater contamination and contamination of soil are not clearly understood. Application of nanomaterials to soil helps in the

Table 4.1 Application of nanoparticles in soil for enhancement

Nanoparticles	Applications in soil	References
Nanoscale zerovalent iron, nanoscale zeolites, metal oxides, carbon nanotubes and fibers, enzymes, various noble metals, and titanium dioxide	Nanoremediation has the potential not only to reduce the overall costs of cleaning up large-scale contaminated sites but also to reduce cleanup time, eliminate the need for treatment and disposal of contaminated soil, and reduce some contaminant concentrations to near-zero: all in situ	Karn et al. (2009)
Nano-additives, nanoclay, nanosilica	Mixture of soil with some nano-additive or nanomaterial or nanoparticle could improve the soil strength parameters and stabilize and improve weak soils. Due to a very high specific surface area of nanomaterials, surface charges and their morphologic properties, nanomaterial in the soil could influence significantly the physical and chemical behavior of soil.	Arya and Jain (2017)
Na + modified montmorillonite, used as nanoclay	The results suggested that plastic and liquid limits can be increased by adding nanoclay into the soil. This variation was greater in plastic one. Given the results of unconfined compressive strength on nanoclay samples, the soil containing 1.5% of nanoclay has the greatest resistivity. Increasing nanoclay content from 1.5% to 2% reduces the ultimate compressive strength. Nanoclay due to high specific surface area makes a major impact on soil engineering properties, and so little percentage of this material can be used to achieve better results.	Nohani and Alimakan (2015)
Titanium oxide nanoparticles	Shear strength and consolidation of soil decrease, thus reducing the maintenance cost and structure failure. Greater improvement in California bearing ratio value was found on adding nano-TiO_2 compared to nanoflyash, thus making it more useful for pavement works over nanoflyash.	Babu and Joseph (2015)
Soil nanoparticles like clay	Soils containing nanoparticles with nanoscale intraparticle voids usually exhibit much higher liquid and plastic limits that usually show irreversible changes upon drying, while the	Zhang (2007)

(continued)

Table 4.1 (continued)

Nanoparticles	Applications in soil	References
	presence of fibrous nanoparticles usually makes the soil more thixotropic and enhances its shear strength	
Nanoclay, nanoalumina, and nanocopper	It was found that with the addition of optimum percentage of nanomaterial, both the swell strain and shrinkage strain reduced. The results show that nanomaterial decreases the development of desiccation cracks on the surface of compacted samples without decrease in the hydraulic conductivity	Taha and Taha (2012)
Nanosilica	It was found that with the addition of the nanosilica to weak soil, the shear strength increased, and California bearing ratio strength and moisture % also increased. The presence of only small amount of nanomaterial in the soil influenced significantly the physical and chemical behavior of soil due to a very high specific surface area of nanomaterials, surface charges, and their morphologic properties.	Alireza et al. 2013
Nanosilica	Compaction characteristics and consistency of the soil were improved by addition of nanosilica: Compressive strength of the soil increased, but hydraulic conductivity and pH decreased	Bahmani et al. (2014)
Nanosilica	Addition of the cement and nanosilica improved the engineering properties of sands. The presence of nanosilica in optimal percentages significantly improved the mechanical properties of cement sand	Choobbasti et al. (2015)
Nanosoil particles	The laboratories result showed that the addition of 2%, 3%, and 4% nanosoil into soft soil improved the soil strength and effective shear strength of stabilized soft soil. Meanwhile the plasticity value decreased after addition of 2%, 3%, and 4% nanosoil, indicating an improvement in the soil. The results showed the small amount of nanosoil can improve and enhance the geotechnical properties of soft soils	Khalid et al. (2015)

(continued)

Table 4.1 (continued)

Nanoparticles	Applications in soil	References
Nanoscale zerovalent iron	Application of nanomaterial with soil can remove large amounts of at the maximum 97% of Cu present in the Cu-contaminated soil	Wan Yaacob et al. (2012)
Fe-Pd nanoparticles	Stabilized nanoparticles displayed markedly improved stability against aggregation, chemical reactivity, and soil transport	He et al. (2007)
Manganese oxide nanoparticles	Stabilized MnO_2 nanoparticles facilitated in situ oxidative degradation of various emerging contaminants in soil and groundwater	Han et al. (2015)
Iron nanoparticles	The stabilized zerovalent iron nanoparticles served as a highly soil-dispersible and effective agent for in situ reductive immobilization of chromium in soils, groundwater, or industrial wastes	Xu and Zhao (2007)
Nanoscale zerovalent iron	Starch-stabilized ZVI nanoparticles facilitated in situ immobilization of perrhenate (ReO_4^-) in soil and groundwater	Liu et al. (2013)
Iron sulfide nanoparticles	In situ immobilization of Hg	Gong et al. (2012)
Magnetite nanoparticles	Immobilization and removal of phosphorus (P) in soils	Pan et al. (2010)
Iron phosphate nanoparticles	Compared to soluble phosphate used for in situ metal immobilization, application of the iron phosphate nanoparticles results in ~50% reduction in phosphate leaching into the environment	Liu and Zhao (2007)
Iron sulfide nanoparticles	Immobilization and removal of mercury in soils. The immobilized mercury remained stable when preserved for 2.5 years at pH above neutral	Gong et al. (2014)
Amphiphilic polyurethane (APU) nanoparticles	The mobility of colloidal APU suspensions in soil is controlled by the charge density or the size of the pendent water-soluble chains that reside on the particle surface. Exemplary results were provided illustrating the influence of alternative APU particle formulations with respect to their efficiency for contaminant removal. The ability to control particle properties offers the potential to produce different nanoparticles optimized for	Tungittiplakorn et al. (2004)

(continued)

Table 4.1 (continued)

Nanoparticles	Applications in soil	References
	varying contaminant types and soil conditions	
Iron sulfide nanoparticles	Immobilization and removal of mercury in soils	Xiong et al. (2009)
Iron nanoparticles	Carboxymethyl cellulose (CMC) stabilized zerovalent iron (ZVI) nanoparticles (with a trace amount of Pd catalyst) for in situ destruction of chlorinated ethenes such as perchloroethylene (PCE) and trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) that had been in groundwater	He et al. (2010)

enhancement of soil properties and greatly improves its mechanical and structural properties. Table 4.1 lists the application of few nanomaterials for enhancement in soil.

Although there have been few studies regarding the fate of these nanoparticles in soil, water, and wastewater, there is still a major knowledge gap regarding the fate and transport of these nanoparticles deposited in the soil.

The aim of this study was to improve understanding on long-term interactions of nanomaterials with natural and undisturbed soil during land application of nanomaterial-contaminated sludge and to identify factors which affect their transport and mobility. This information will be useful in improving the understanding on effect of sludge on soil after land application with regards to the mixture of nanomaterials and to know its potential of groundwater contamination. Finally, it will help in deciding whether the practices of land application of contaminated sludge as soil-amendment materials are safe to soil environment and to groundwater.

4.2 Methodology

This study aimed to review the following aspects: (1) adsorption of mixture of nanomaterials on solids, (2) leaching patterns of mixture of nanomaterials from solids, (3) fate and transport of leached nanomaterials in soils, and (4) fate and transport of leached nanomaterials in soil in field lysimeter studies for understanding the current status of knowledge and for identifying knowledge gaps. A detailed literature survey was done using the Science Direct database with different combinations of keywords, such as “nanoparticles, aquatic”; “nanoparticles, interaction”; “nanoparticles, quantification”; “nanoparticles, wastewater”; “nanoparticles, drinking water”; “nanoparticles, potable water”; “nanoparticles, management”; and “nanoparticles removal methods.” For getting detailed understanding, this study focused only on two types of OECD-listed nanoparticles (ENV/JM/MONO/(2015) 15/Part 3, ENV/JM/MONO/(2012) 40): copper oxide nanoparticles (CuO NPs) and

Table 4.2 Information on occurrence of CuO and ZnO nanoparticles in different matrices

Nanoparticles	Raw wastewater (μg/L)		Effluent wastewater (μg/l)		Sludge (dry weight) (mg/kg)		Surface water (μg/L)	
	Monitored	Simulated$^{\#,*}$	Monitored	Simulated	Monitored	Simulated$^{\#,*}$	Monitored	Simulated$^{\#,*}$
CuO	1.4	NR	NR	NR	NR	NR	60–68	NR
ZnO	5.6	NR	0.089–5.29	0.340–1.42	7–39.8	13.6–57.0	71–74	0.008–0.055

Source: OECD Environment, Health and Safety Publications Series on Pollutant Release and Transfer Registers, No. 16 Global Pollutant Release and Transfer Register and Project on Emerging Nanotechnologies (2014; Consumer Products Inventory 2015; Kirkegaard et al. 2015; Aitken et al. 2006; Kiser et al. 2010; Westerhoff et al. 2011; Hou et al. 2012; Chalew et al. 2013; Blaser et al. 2008). Simulated values reported from Gottschalk et al. (2009) and Mueller and Nowack (2008)

All monitored values are reported in terms of metal concentrations

NR not reported

: Gottschalk et al. (2009)

* : Mueller and Nowack (2008)

zinc oxide nanoparticles (ZnO NPs) as these nanoparticles have been used for various commercial purposes (the usage percentage of the nanoparticles was reported as ZnO (9%) and CuO (6%); Consumer Products Inventory 2015). Considering the rapid and continuous increase in the production and use of these two nanoparticles, its environmental concentration is expected to inevitably increase (Table 4.2). In municipal wastewater, its concentration is likely to be in mg/L level in the next few years (Tan et al. 2015). These aspects indicate the need for developing detailed understanding on environmental fate of these nanoparticles and their impacts on environment. The following sections present detailed information on different aspects which highlights currently available knowledge and present knowledge gaps as well.

4.3 Fate and Transport of Nanoparticles in Column Studies

Soil is an important sink for engineered nanomaterials after their release into the environment and a possible source of groundwater contamination. Understanding the transport behavior of engineered nanomaterials in natural soil systems is essential to reveal their potential impacts on groundwater. In addition, many environmental applications of engineered nanomaterials to clean up groundwater need information on their transport (e.g., zerovalent iron nanoparticles) through soil and/or sediment (He et al. 2007; Schrick et al. 2004). Therefore, transport of these metal oxide nanoparticles in sand media and soils have attracted increased research attention (Liu et al. 2009). Transport of particles in the porous media depends largely on the rate of their capture or filtration by the stationary grain surfaces. Particle filtration theory can be used to help understand the transport behavior of nanoparticles in soil. There are three basic mechanisms for describing capture of colloidal particles in porous media: gravitational sedimentation, interception, and Brownian diffusion.

Table 4.3 presents summaries of findings of some of the column studies which focused on fate and retention of engineered nanomaterials in porous medium. Currently, information is available on interaction of nanomaterials with soil particles where fate of nanomaterials in soil and its fate in a vertical soil column are characterized. Studies have focused on column prepared using repacked, homogenous, porous media for understanding mechanisms for nanomaterial removal. For example, a recent paper had focused on studying transport of functionalized multi-walled carbon nanotubes in natural soils (column and lysimeter studies) (Kasel et al. 2013) and reported no breakthrough and recovery of multi-walled carbon nanotubes (MWCNTs) in soil with higher retention near the column or lysimeter inlet.

Carstens et al. (2017) studied the effect of flow interruption on transport and retention of negatively charged organic matter-coated goethite colloids in saturated quartz sand column under continuous and saturated flow conditions and observed that colloids were very mobile in continuous flow conditions. During flow interruptions, significant amounts of iron oxide colloids were retained in solid matrix and could not be mobilized after resumption of flow. Studies indicated the need for conducting studies in natural soil where interruption of flow is more probable which can increase the retention of colloids in porous medium (Fig. 4.1).

Table 4.3 Summary of column studies focused on fate and transport of nanoparticles

References	Material	Metal/nanoparticles	Co-transport study
Gabaldon et al. (2000)	Activated carbon	Metal ions	No
Solovitch et al. (2010)	Sand	32 nm TiO_2 nanoparticles	No
Torkzaban et al. (2008)	Sand	10 nm colloids	No
Shani et al. (2008)	Sand	20 nm colloids	No
Bradford et al. (2002)	Sand	15 nm Al	No
Doshi et al. (2008)	Sand	1–10 µm Al nanoparticles	No
Waznea et al. (2008)	Quartz sand	10–20 nm Bo nanoparticles	No
Jones and Su (2012)	Quartz sand	25 nm Cu nanoparticles	No
Inyang et al. (2013)	Activated carbon with Iron chips	50 nm Ag nanoprticles; 92 nm Ti nanoparticles; 140 nm carbon nanotubes	No
Godinez and Darnault (2011)	Silica	21 nm Ti nanoparticles	No
He et al. (2009)	Glass beads, Sandy soil	20 nm iron	No
Chowdhury et al. (2011)	Quartz sand	20 nm titanium	No
Pavlova-Verevkina et al. (2009)	Sand	6–7 nm TiO_2 nanoparticles	No
Domingos et al. (2009)	Sand	5 nm TiO_2 nanoparticles	No
French et al. (2009)	Quartz sand	4–6 nm TiO_2 nanoparticles	No
Fang et al. (2009)	Sand	35 nm TiO_2 nanoparticles	No
Pettibone et al. (2008)	Quartz sand	5–32 nm TiO_2 nanoparticles	No
Tseng and Lin (2003)	Sand	7–20 nm TiO_2 nanoparticles	No
Godinez et al. (2013)	Silica sand	19 nm titanium	No
Kasel et al. (2013)	Natural soils	Multi-walled carbon nanotube (MWCNT)	No
Kasel et al. (2013) (lysimeter study)	Natural soils	Multi-walled carbon nanotube (MWCNT)	No
Syngouna and Chrysikopoulos (2013)	Glass beads	Viruses (bacteriophages MS2 and ΦX174) and clay (kaolinite and montmorillonite)	Co-transport study

(continued)

Table 4.3 (continued)

References	Material	Metal/nanoparticles	Co-transport study
Syngouna and Chrysikopoulos (2015)	Glass beads	Bacteriophages MS2 and ΦX174; clay	Co-transport study
Walshe et al. (2010)	Gravel aquifer	MS2 bacteriophages and kaolinite	Co-transport study
Carstens et al. (2017)	Quartz sand	Negatively charged organic matter-coated goethite	No
Seetha et al. (2015a)	Porous medium	Virus and colloids	Co-transport modeling
Seetha et al. (2015b)	Porous medium	Nanoparticles	No co-transport study
Piplai et al. (2018)	Activated carbon	ZnO and CuO nanoparticles	Column co-transport

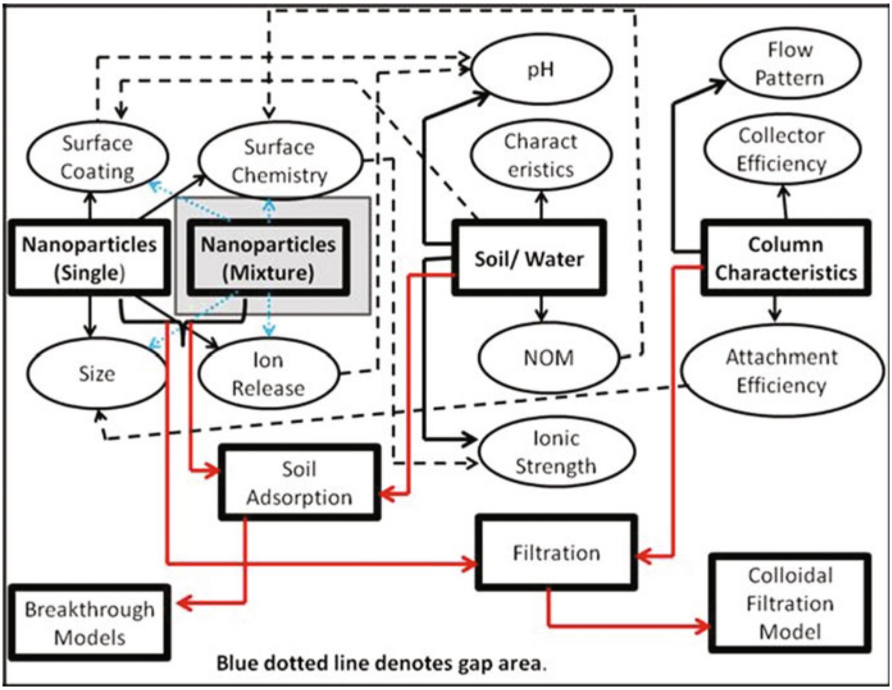


Fig. 4.1 Factors affecting the fate and transport of nanoparticles in porous media (blue line indicates gap areas; dotted line indicates interdependence; *NOM* natural organic matter)

The following sections present detailed analysis of the factors which affect them.

4.4 Factors Affecting the Fate and Transport of Nanoparticles in Column Studies

4.4.1 Water Characteristics

pH

Nanoparticles have different zeta potential values at different pH and thus, their transport behaviors change due to change in surface charge heterogeneities and their interaction with porous medium. Studies from Table 4.2, namely, Pettibone et al. (2008), Domingos et al. (2009), Ho and McKay (1998), and Piplai et al. (2017), analyzed the effect of pH on the fate and transport of nanoparticles. The results for the transport of the ZnO NPs at pH 9 showed significant retention at the inlet of the column containing sand media with hyper-exponential retention profiles regardless of ionic strength values investigated (0.1 and 10 mM) (He et al. 2009; Guzman et al. 2006). The trend was attributed to favorable nanoparticle-nanoparticle interaction and greater surface roughness. During the release tests, ZnO NPs were found to be retained during the continuous injection of particle-free solution at pH 6 (Han et al. 2014; Domingos et al. 2009). However, retained ZnO NPs slowly dissolved and released back into the aqueous phase over time under environmentally-relevant pH conditions (pH value ranging from 5 to 9). The dissolution amount and rate constant values were enhanced at lower pH values that were typical of acidic soils because of enhanced solubility of ZnO NPs; this trend was mainly attributed to the strong re-adsorption of the released Zn^{2+}. Results provided valuable insight for evaluating the dissolution behavior and assessing the risks from ZnO NPs in aquifer environments (Tumin et al. 2008; Ho and McKay 1998). The results for breakthrough curves and time-lapsed retention profiles showed that reducing solution pH led to the release of large amount of the initially retained ZnO NPs, and the release rate was observed to be greater for bare silica than biofilm-coated sand. The release of ZnO NPs was likely attributed to the dissolution of Zn^{2+} due to the change of pH (Pettibone et al. 2008; Guzman et al. 2006). Similarly, it was noted that the rate-limiting step in the case of Cu^{2+} was chemical sorption happening due the sharing of electrons by valence forces between Cu^{2+} and porous media. Overall, these observations indicated that only the surface phenomena took place between the ions and porous media surface at this stage (Ganesh et al. 2010; Bian et al. 2011). There existed a high potential of complete transport of ZnO NPs into groundwater in soil pore water pH between 5 and 9 (Guzman et al. 2006). It indicated that pH of the percolating water affected the chance of retention of nanoparticles in porous media and release of nanoparticles from porous media. Further studies on the long-term release and dissolution behavior of different toxic metal oxide nanoparticles for different pH ranges are necessary.

Ionic Strength (IS)

Ionic strength of the aqueous media results in either aggregation or stabilization of the nanoparticles and affects their fate and transport in the porous media (Cornelis et al. 2012; Fang et al. 2016). Deposition of nanoparticles has been observed to increase with increasing solution ionic strength in both monovalent and divalent salt solutions. For example, Jiang et al. (2012) investigated the transport behavior of ZnO nanoparticles in quartz sand at different ionic strengths in monovalent and divalent salt solution. Increasing ionic strength (from 1 to 20 mM NaCl concentration) was observed to increase percentage retention from 27.3 to 85.4. Similarly, for divalent solution of $CaCl_{2,}$ retention increased from 42.6 to 75.5 by increasing ionic strength from 0.1 to 1 mM. According to Ben-Moshe et al. (2010), increasing ionic strength increased deposition with only 1.8, 1.5, and 1.2% exiting from column for NaCl concentration of 0.001, 0.01, and 0.1 M, respectively. Higher ionic strength led to increase in the van der Waals forces over repulsive electrostatic interactions, leading to enhanced aggregation. The addition of salt affected stable suspensions more strongly than unstable ones (Ben-Moshe et al. 2010). Both homo-aggregation and hetero-aggregation were enhanced with increase in ionic strength. Increase in ionic strength resulted in compression of electrical double layer, thus decreasing the repulsive barrier between the nanoparticles. Enhancing the ionic strength from 1 mM to 100 mM decreased the zeta potential values of polymerized zerovalent iron from −24.2 mV to −15 mV (Mylon et al. 2004; He and Zhao 2007). With increase of ionic strength from 0 to 50 mM NaCl, breakthrough, i.e., C/Co, decreased, indicating that more graphene oxide nanoparticles were retained in the column with the increase of ionic strength (Qi et al. 2014). With increase in ionic strength, diffuse layer between collector and nanoparticles decreased, thus decreasing repulsion and magnitude of zeta potential (Jones and Su 2012). For developing understanding, studies have attempted to apply the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory for retention of nanoparticles in porous medium and reported application potential for larger nanoparticles (larger than 30 nm) (Keller et al. 2010; Zhang et al. 2008; Limbach et al. 2008). The DLVO theory has been shown to be applicable for the case of adsorption of nanoparticles on soil particle surfaces (or hetero-aggregation), as it describes the interaction energy between nanoparticles and a collector surface as well as the stability of the nanomaterials in suspension.

Natural Organic Matter (NOM)

Natural organic matter (NOM), which is mainly comprised of humic and fulvic substances, is ubiquitous in natural aqueous environments. The natural soil environment is physically, biologically, and geochemically heterogeneous, and the presence of NOM and minerals and changing soil chemistry can influence the nanoparticle transport. Natural organic matter has been found to enhance the transportability of nanoparticles in porous media due to the increased charge and/or steric stabilization (Pelley and Tufenkji 2008; Jaisi et al. 2008; Johnson et al. 2011). Natural organic matter attaches itself to the surface of the metal oxide nanoparticles, like ZnO NPs and CuO NPs, changing the physiochemical properties of nanoparticles and the interfacial forces or energies between interacting nanoparticles, thereby, altering the aggregation behavior of particles (Louie et al. 2015). There is an increase in the aggregation of ZnO NPs and CuO NPs with the increasing ionic strength. However, this trend could go in the opposite direction with the addition of humic acid (HA) (up to 3 mg/L). Nanoparticles coated with natural organic matter had slow aggregation even at high ionic strengths (Zhou and Keller 2010). The effect of humic acid (HA) on metal oxide nanoparticle aggregation is related to ionic strength and electrolyte type. For example, at low concentrations (0.004 M) of $CaCl_2$, humic acid inhibited aggregation of CeO_2 NPs and ZnO NPs; however, humic acid enhances aggregation of particles at high concentrations (0.08 M) of $CaCl_2$. The sedimentation rate of ZnO NPs was found to be higher at the lowest dissolved humic acid concentration (1.7 mg/L) than the sedimentation rate in the absence of humic acid (Wang et al. 2015). In addition, the influence of humic acid on the nanoparticle agglomeration strongly depended on the reaction time (Zhu et al. 2014). It was determined that humic acid can affect the stability of CuO NPs via steric hindrance, charge neutralization and bridging effects (Bian et al. 2011). The structure and conformation of natural organic matter can also be influenced by the solution pH, since electrostatic repulsion of the ionizable functional groups of the natural organic matter (carboxylic and phenolic groups) can result in the particles becoming more flexible and expanded at high pH or low ionic concentrations and more rigid and compact at low pH or high ionic concentrations (Cornelis et al. 2014; Zhang et al. 2013). The majority of studies have shown that the presence of natural organic matter can increase the stability of metal oxide nanoparticles like ZnO NPs and CuO NPs, even in the presence of high concentrations of salts, such as NaCl and KCl. However, this aspect has not often been observed for divalent ions (such as Ca^{2+} and Mg^{2+}) present at levels exceeding the critical coagulation concentration (Mashayekhi et al. 2012). The association between these selected metal oxide nanoparticles and natural organic matter resulted in modification of the interactions, transport, fate, and toxicity of nanoparticles. Natural organic matter (and the humic substance (HS), humic acid (HA), and fulvic acid (FA) fractions) acts to diminish aggregation of the nanoparticles, which increased their stability. Organic matter alters surface charge, thus, affecting particle stability and aggregate size. However, almost no field experiment has been performed to investigate the transport of engineered nanomaterials in natural soils or sediments. Specific mechanisms for the transport enhancement of natural organic matter remain unclear. Future research should be directed to clarify the interaction of engineered nanomaterials with soil components (e.g., natural organic matter and clay minerals) and its effect on migration of nanoparticles in soil pores. Further work is required to elucidate the dynamics of the interactions between engineered nanomaterials and natural organic matter, as well as the mechanisms of stabilization and aggregation of these particles in the environment.

4.4.2 Nanoparticle Characteristics

Surface Coating

Surface coating has been shown to affect fate and transport of nanoparticles in a porous medium. Due to the varying chemical compositions of nanoparticles and the possibility of "tuning" the specific properties of nanoparticles, the effect of surface coating on fate and transport of nanoparticles cannot be generalized. Some studies have reported that surface coating might enhance mobility of nanoparticles, and some studies have reported another type of observation. Bare ZnO and CuO nanoparticles have very limited transport distances and low bio-availability in natural soils in a short exposure time, because most of the nanoparticles are associated or complexed with various soil components (Ryan and Elimelech 1996). Given that a majority of commercially and industrially employed nanoparticles, like ZnO NPs and CuO NPs, are surface-functionalized, stabilized, or matrix embedded, various derivatives of these basic metal oxide nanoparticle types may exhibit far greater mobility upon release. For example, Jaisi et al. (2008) observed that surface coating of ZnO nanoparticles increased its mobility in the soil column from 68% to 99% and attributed to physical retention, as the grains in the soil have irregular shape and rough surface. Results also have shown that capped ZnO and CuO nanoparticles can travel farther than uncoated ZnO and CuO nanoparticles; thus, they may have a potential impact on groundwater and plants. Surface modification leads to increase in mobility and stability of nanoparticles. For example, the study conducted by Zhao et al. (2012) showed that the distances traveled by bare ZnO nanoparticles and coated ZnO nanoparticles in sandy and sandy loamy soil were observed to be 19.3,5.3 and 21.4,6.9 cm, respectively. The surface coating on nanoparticles reduced deposition rates from 0.73 to 0.65 and from 2.28 to 1.74 for sandy soil and sandy loamy soil, respectively. This indicates that the reason behind the effect of surface coating on nanoparticles and soil type on retention, mobility, and deposition of nanoparticle which can be attributed to the effect of electrostatic and steric repulsion between the nanoparticles surface and the coating or soil type provided. Under all examined conditions, nanoparticles are mainly retained at segments near the column inlet. The retained metal oxide nanoparticle concentrations versus transport distance decreased faster than the theoretical prediction of log-linear decrease under all examined conditions. Another aspect is the interaction of the surface constituent on nanoparticles with surface functional groups on soil which might affect the mobility of nanoparticles. For example, Johnson and Elimelech (1995) observed that a small quantity of iron oxide coating helped in the deposition of negatively charged surface of modified ZnO nanoparticles.

A majority of the aggregation and deposition studies conducted till date have involved bare, non-functionalized nanomaterials. However, nanoparticles released into the environment may be either matrix-bound or functionalized, thus altering their behavior. For example, particles may undergo redox reactions or become coated with organic matter. Both chemical and biological processes may result in inadvertent surface functionalization (Chang et al. 2004). On the other hand, such processes may wear down or alter existing surface functionality and particle coatings (Bailey and Nie 2003). In the aim of understanding and predicting nanoparticles' fate in aqueous environments, an in-depth characterization of particle surfaces following functionalization is necessary. Regardless of prior characterization, additional particle modifications and chemical transformations can also occur upon release into the environment.

Size

The size of nanoparticles depends on different factors, such as coating on nanoparticles, aqueous chemistry, etc. and has been reported to affect fate and transport of nanoparticles in porous medium. Studies have shown that large-sized nanoparticles are retained lesser in a soil column than small-sized nanoparticles. Wang et al. (2012) explained this aspect using the DLVO theory and attributed to the effect of interaction energy between the nanoparticles and the sand matrix. Furthermore, it was concluded that DLVO theory could not account for behavior of the smaller nanoparticles (diameter = 8 nm), possibly due to short-range interactions, e.g., hydration and solvation. Further, another study (Jeong and Kim. 2009) revealed significant differences in particle deposition rates for different-sized nanoparticles. The observed variation in particle attachment behavior was attributed to deposition in the secondary energy well, which becomes more significant with increasing particle size. The transport of nanoscale colloids was theoretically predicted to decrease with increasing particle size (Elimelech et al. 1995). However, nanoparticles are prone to form large aggregates, which can greatly inhibit their transport, thus becoming an important component of particle capture (Hydutsky et al. 2007; Darlington et al. 2009).

A number of researchers have revealed that dispersed metal oxide nanoparticles, like ZnO NPs and CuO NPs, can transport through porous media, while, the pristine engineered nanomaterials are prone to form aggregates and are filtered by the grains (He et al. 2007; Kanel et al. 2008; Saleh et al. 2008; Schrick et al. 2004; Yang et al. 2007). However, to date, there are different understandings and opinions about the effect of size of nanoparticles on their transport in porous media. Schrick et al. (2004), for example, calculated the filtration length of metal oxide nanoparticles through sand and soil columns, indicating that 30–100 nm diameter particles had poor transport properties compared to particles in diameters ranging from 400 to 500 nm. Further, metal oxide nanoparticles, like ZnO NPs and CuO NPs, may aggregate to become microscale particles, which can be retained by the media due to physical screening if the size of the aggregate is larger than the pore through which fluid is flowing (Gajjar et al. 2009). The capture or filtration of particles by the collector surfaces is determined by the chemical-colloidal interaction between particles and surface, which, in turn, is regulated by solution chemistry (e.g., pH, ionic strength, and co-existing organic matters) and chemical characteristics of particles and surfaces. Physical parameters, such as particle size, fluid velocity, grain size, and water temperature can also play important roles in the filtration of the engineered nanomaterials (Dimkpa et al. 2011). The transport of these nanoparticles is more complex than microscale particles because of their tendency to aggregate, which strongly depends on particle size in the nanoscale regime. In contrast, Pelley and Tufenkji (2008) pointed out that at low ionic strengths, the attachment efficiency between latex particles and quartz sand collectors increased with increasing particle size, i.e., the migration of latex particles decreased with the increase in particle size. The change of particle filtration with particle size can also result in complex effects, because some properties, such as charge, surface energy, and particle morphology, can also have an effect on the particle size (Elimelech et al. 1995). Particle (or soil) morphology might affect the transport behavior. However, very few experimental studies have been designed to reveal the effect of particle morphology on the transport of nanoparticles in porous media. More studies are required to understand this aspect. Also, unusual particle shapes might give rise to additional capture mechanisms (e.g., straining) which might result in unpredicted nanomaterials transport patterns and thus need to be studied in detail.

Many of these same challenges apply when considering nanoparticle aggregation and deposition in natural settings, given that, an in-depth particle characterization is required to fully understand particle mobility. Most deposition and aggregation studies have been conducted with simplified model laboratory systems. However, while providing important insights, particle behavior in model laboratory systems might not be representative of that observed in far more complex natural environments. Bridging due to the adsorption of certain polymers onto particle surfaces can result in heightened aggregation. Most common experimental and theoretical approaches used for evaluation of nanomaterial deposition and aggregation are applicable for spherical particles only. Quantification and limited knowledge are major impediments in this area. Also, major knowledge gap arises due to a lack of analytical tools capable of characterizing and quantifying nanoparticles in complex environmental matrices which needs to be worked upon and addressed at the earliest.

Surface Chemistry

Surface chemistry of ZnO NPs and CuO NPs is another key factor that can control the mobility of these nanoparticles in porous media. Generally, hydrophobic surface of nanoparticles will lead to nanoparticle aggregation and sedimentation out of the flowing solution, while engineered nanomaterials with hydrophilic surface can be relatively easily dispersed and transported with the water flow (Hotze et al. 2010). Surface charge is another important property that can dominate the migration of ZnO NPs and CuO NPs in porous media (Darlington et al. 2009). Thus, positively charged engineered nanomaterials will be readily electrostatically attracted to the soil surface. This trend was also explained earlier in the case of activated carbon media (Piplai et al. 2017). Both the nanoparticles with such higher negative charges are believed to be more mobile in soil matrix because of the stronger electrostatic repulsion between the nanoparticles and soil particles and between nanoparticles themselves as well. Therefore, various methods have been applied to modify the

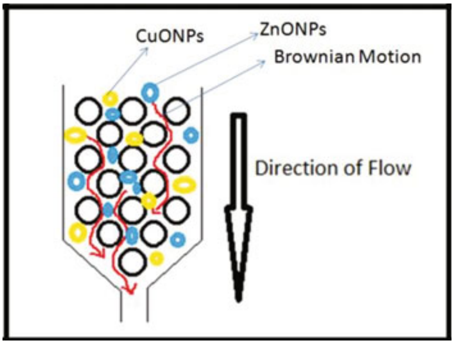


Fig. 4.2 Schematic representation of the effect of flow transport parameters in a column (ZnO NPs, zinc oxide nanoparticles; CuO NPs, copper oxide nanoparticles)

nanoparticle surface properties to control (enhance or restrict) their transport in porous media, among which surface functionalization with hydrophilic functional groups (e.g., − OH and –COOH) and surface physical modification using polymers or surfactants are two commonly adopted methods (Phenrat et al. 2008; Hotze et al. 2010). Investigations into the mobility of these two nanoparticles in porous media have shown that altering the surface functional groups of nanoparticles can result in significant differences in their transportability due to the increased hydrophilicity and/or surface charge (Pelley and Tufenkji 2008). Solution pH controls the solubility of these metal-based nanoparticles and their surface charges and thus also the electrostatic interactions between nanoparticles and between nanoparticles and porous media (Doshi et al. 2008).

Temperature is another solution property that influences the transport of these metal oxide nanoparticles like ZnO NPs and CuO NPs in porous media. Elimelech et al. (1995) analyzed the effect of solution temperature on particle migration in soils and aquifers, indicating that transportability of these nanoparticles decreases with the increase in solution temperature because high temperature increases the Brownian motion (Fig. 4.2) of colloids and thus enhances the capture of these particles by the media particles.

It is a known fact that nanoparticles are unstable, and after undergoing reactions due to varied surface chemistry properties, they also undergo a transformation that will dramatically affect their size distribution and surface properties. However, understanding these various aggregation or disaggregation reactions to clearly understand the surface properties of these metal oxide nanoparticles remains the most difficult task so far and needs to be worked on.

Mixture of Nanoparticles

Effects of solution chemistry (pH, ionic strength), soil type, flow rate, surfactant, natural organic matter, and nanoparticle concentration have been observed in the transport of nanoparticles in porous media as seen from Table 4.1. These studies focused on single nanoparticle transport. However, since more than one nanoparticle

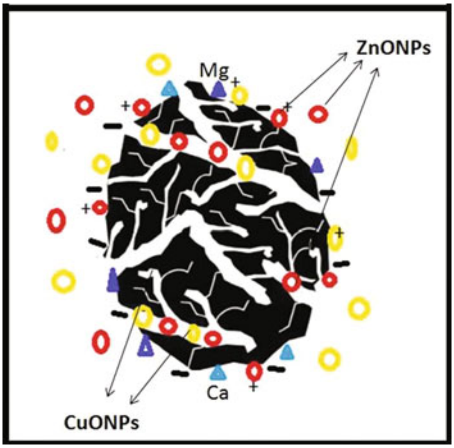


Fig. 4.3 Schematic representation of the effect of ions and co-solutes in soil media (ZnO NPs, zinc oxide nanoparticles; CuO NPs, copper oxide nanoparticles)

are getting into landfill or soil, there are high chances of simultaneous release of nanoparticles into soil and ultimately into groundwater. There is a need to investigate the effects mentioned above with respect to co-transport of nanomaterials. However, very few researchers are working on understanding the fate of engineered nanomaterials in porous medium during co-transport of more than one type of engineered nanomaterials and/or mixture of inert and biocolloids or on understanding interaction with porous medium in batch studies. Figure 4.3 illustrates a schematic representation of the effect of the ions along with the co-solutes that are present in the soil on the fate and transport of the metal oxide nanoparticles.

Studies focusing on co-transport of metal oxide nanoparticles in porous media are very scarce and pose to be a big knowledge gap. Much of what is understood or proposed is derived from experience with colloidal particles or metals.

Some studies have focused on understanding the effect of colloids on contaminant transport in porous media as well as on understanding co-transport of biocolloids with colloids. For example, Syngouna and Chrysikopoulos (2013) studied co-transport of clay colloids and viruses in water-saturated porous media in laboratory columns and examined the combined effects of clay colloids and pore water velocity on virus transport and retention in porous media. They reported that mass recovery of viruses and extent of virus transport values were observed to decrease compared to those in the absence of clays indicating the effect of clay on retention of viruses. Further, Seetha et al. (2015a) modeled the co-transport of viruses and colloids in unsaturated porous media using experimental data from literature (Syngouna and Chrysikopoulos 2013; Walshe et al. 2010) and reported good agreement and fitted breakthrough curves under both saturated and unsaturated conditions. In another study, Seetha et al. (2015b) developed correlation equations for determining average deposition rate coefficients of nanoparticles in a cylindrical pore as a function of nine pore-scale parameters. However, these studies have not focused on understanding the fate of engineered nanomaterials in sand or soil during co-transport of engineered nanomaterials which might be a realistic case given the possibility of contamination of sludge with different types of engineered nanomaterials. In this direction, two types of studies have been recently done: one focusing on interaction of mixture of ZnO and CuO nanoparticles with activated carbon in batch studies (Piplai et al. 2017) and another study (Piplai et al. 2018) which compared removal and transport of two types of nanoparticles in an activated carbon column bed. In the batch study, Piplai et al. (2017) studied the effects of pH and activated carbon (AC) concentration on the removal of a colloidal solution of nanoparticles (NPs) (ZnO + CuO) using activated carbon in batch kinetic studies. They observed that in a colloidal solution containing mixture of zinc oxide nanoparticles (ZnO NPs) and copper oxide nanoparticles (CuO NPs), adsorption capacity of activated carbon (AC) for Zn in deionized water was 0.71 ± 0.051 mg/g (74.7% removal) and in wastewater was 0.576 ± 0.019 mg/g (69% removal) and for Cu in deionized water was 0.82 ± 0.017 mg/g (81.2% removal) and in wastewater was 0.6 ± 0.032 mg/g (71.5% removal). Further, in column study, they observed that superficial velocity, concentration of engineered nanoparticles, and different types of nanoparticles influenced the removal at room temperature (p-value lesser than 0.05). Ninety percent removal of ZnO NP and CuO NP, for both single and binary suspensions, were achieved for a concentration of 1 mg/L and 10 mg/L of ZnO NPs and CuO NPs. They noticed that the breakthrough was reached faster for total Cu and Zn in binary mixture of nanoparticles than in single nanoparticle suspension. These types of information are required for natural soils, so that its implications on soil contamination and groundwater contamination can be studied. Overall, the above mentioned studies indicated that efforts have been started for studying the fate and transport of mixture of nanoparticles; however, none of these studies focus on the co-transport of engineered nanomaterials in natural soils. Further work is required for getting more understanding in this direction.

4.5 Conclusion

This study presented a summary of findings of column studies focusing on fate and transport of nanoparticles. Even when considering one type of particle, several factors complicate comparison among studies. These factors are variability in particle size and concentration, water chemistry (i.e., electrolyte species, ionic strength, and pH), flow velocity, and choice of collector surface. Out of the two nanoparticles selected for this study, CuO nanoparticles hardly have data regarding its fate and transport in sand or soil columns. A very limited number of nanoparticles have been studied like TiO_2, Ag, etc. The effect of co-solutes on the transport of nanoparticles in soil or porous media still needs to be addressed. Moreover, given the importance of particle surface properties, direct comparisons between experiments involving bare and surface-modified nanoparticles are difficult to make. It is essential to elucidate which physicochemical interactions govern particle-surface and particle-particle interactions under conditions representative of the aquatic environments. While a great deal of work analyzing the behavior of micrometer-sized particles in various aquatic environments has been performed, limited data (and quantitative analysis) are available for nano-sized particles, both in terms of aggregation and deposition. Overall, there are many unknowns regarding the environmental fate, transport, exposure, ecotoxicity, and life cycle of nanoparticles. It is necessary to define and understand the environmental and health impacts of the nanoparticles for the development and understanding of the environment and the system. Further, similar information about the fate of mixture of metal oxide nanoparticles in soil is also not available. It is important to study co-transport of engineered nanomaterials in porous medium as environmental media are expected to contain more than one type of engineered nanomaterials, which might lead to different fate and transport of different engineered nanomaterials and their associated ions through porous medium. Although some studies have focused on this aspect, none of these studies have focused on understanding the effect of co-transport of engineered nanomaterials in porous medium like natural soil, sand, etc. on their retention and breakthrough profiles. Further it is also important to know how this condition influences column operating parameters.

The following actions need to be taken to address the knowledge gaps identified:

1. Conduct short-term and long-term studies at laboratory scale for predicting the behavior of mixture of nanoparticles in natural soil condition by varying environmental realistic parameters like ionic strength, natural organic matter, nanoparticle concentration, and flow rate.
2. Conduct experiments delineating mechanism/factors of deposition and mobility of nanoparticles; consider combined effects of all the parameters leading to nanoparticle retention during calculation of particle collision/attachment efficiency.

Acknowledgment The authors would like to thank the Indian Institutes of Technology (IIT), Delhi, for providing all facilities and financial assistance to carry out this work.

References

Aitken RJ, Chaudhry MQ, Boxall ABA, Hull M (2006) Manufacture and use of nanomaterials: current status in the UK and global trends. Occup Med 56(5):300–306

Alireza S, Hasan BM, Gelsefidi S, Mohammad MS (2013) Application of nanomaterial to stabilize a weak soil. International conference on case histories in geotechnical engineering, Paper 5

Arya A, JainA (2017) A review of geotechnical characteristics of nano additives treated soils. International conference on recent developments in engineering science. Humanities and Management, Chandigarh. ISBN:978-93-86171-25-2

Babu S, Joseph S (2015) Effect of nano materials on properties of soft soil. Int J Sci Res (IJSR); ISSN (Online): 2319–7064

Bahmani SH, Bujang BK, Asadi H, Farzadnia A, N. (2014) Stabilization of residual soil using SiO2 Nano particles and cement. Constr Build Mater 64:350–359

Bailey RE, Nie SM (2003) Alloyed semiconductor quantum dots: tuning the optical properties without changing the particle size. J Am Chem Soc 125:7100–7106

Ben-Moshe T, Dror I, Berkowitz B (2010) Transport of metal oxide nanoparticles in saturated porous media. Chemosphere 8(13):387–393

Benn TM, Westerhoff P (2008) Nanoparticle silver released into water from ecommercially available sock fabrics. Environ Sci Technol 42(11):4133–4139

Bian SW, Mudunkotuwa IA, Rupasinghe T, Grassian VH (2011) Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: influence of pH, ionic strength, size, and adsorption of humic acid. Langmuir 27(10):6059–6068

Blaser SA, Scheringer M, MacLeod M, Hungerbuhler K (2008) Estimation of cumulative aquatic exposure and risk due to silver: contribution of nanofunctionalized plastics and textiles. Sci Total Environ 390:396–409

Bradford SA, Yates SR, Bettahar M, Simunek J (2002) Physical factors affecting the transport and fate of colloids in saturated porous media. Water Resour Res 38(12):63-1–63-12

Carstens JF, Bachmann J, Neuweiler I (2017) Effects of flow interruption on transport and retention of iron oxide colloids in quartz sand. Coll Surf A Phys Eng Asp 520:532–543

Chalew ATE, Ajmani GS, Huang H, Schwab KJ (2013) Evaluating nanoparticle breakthrough during drinking water treatment. Environ Health Perspect 121(10):1161–1166

Chang S, Zhou M, Grover CP (2004) Information coding and retrieving using fluorescent semiconductor nanocrystals for object identification. Opt Express 12:143–148

Choobbasti AJ, Vafaei A, Kutanaei SS (2015) Mechanical properties of Sandy soil improved with cement and nanosilica. Open Eng J 5(1):111–116

Chowdhury I, Hong Y, Honda RJ, Walker SL (2011) Mechanisms of TiO_2 nanoparticle transport in porous media: role of solution chemistry, nanoparticle concentration, and flowrate. J Colloid Interface Sci 360(2):548–555

Consumer Products Inventory (2015) The project on emerging nanotechnologies; Woodrow Wilson International Center for Scholars

Cornelis G, Doolette C, Thomas M, McLaughlin MJ, Kirby JK, Beak DG, Chittleborough D (2012) 704 retention and dissolution of engineered silver nanoparticles in natural soils. Soil Sci Soc Am J 76:891–902

Cornelis G, Rinke-Hind K, Kuhlbusch T, Brink N, Nickel C (2014) Fate and bioavailability of engineered nanoparticles in soils: a review. Crit Rev Environ Sci Technol 44(24):2720–2764

Darlington TK, Neigh AM, Spencer MT, Nguyen OT, Oldenburg SJ (2009) Nanoparticle characteristics affecting environmental fate and transport through soil. Environ Toxicol Chem 28:1191–1199

Dimkpa CO, Calder A, McLean JE, Britt DW, Anderson AJ (2011) Responses of a soil bacterium, Pseudomonas chlororaphis O6 to commercial metal oxide nanoparticles compared with responses to metal ions. Environ Pollut 159:1749–1756

Domingos RF, Tufenkji N, Wilkinson KJ (2009) Aggregation of titanium dioxide nanoparticles: role of a fulvic acid. Environ Sci Technol 43(5):1282–1286

Doshi R, Braida W, Christodoulatos C, Wazne M, O'Connor G (2008) Nanoaluminum: transport through sand columns and environmental effects on plants and soil communities. Environ Res 106:296–303

Elimelech M, Gregory J, Jia X, Williams RA (1995) Particle deposition and aggregation: measurement, modeling, and simulation. Butterworth-Heinemann, Oxford

ENV/JM/MONO/(2012) 40

ENV/JM/MONO/(2015)15/Part 3

Fang J, Shan X, Wen B, Lin J, Owens G (2009) Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. Environ Pollut 157(4):1101–1109

Fang J, Zhang K, Sun P, Lin D, Shen B, Luo Y (2016) Co-transport of Pb^{2+} and TiO_2 nanoparticles in repacked homogeneous soil columns under saturation condition: effect of ionic strength and fulvic acid. Sci Total Environ. Elsevier B.V. 571:471–478

French RA, Jacobson AR, Kim B, Isley SL, Penn L, Baveye PC (2009) Influence of ionic strength, pH, and cation valence on aggregation kinetics of titanium dioxide nanoparticles. Environ Sci Technol 43(5):1354–1359

Gabaldón C, Marzal P, Seco A, Gonzalez JA (2000) Cadmium and copper removal by a granular activated carbon in laboratory column systems cadmium and copper removal by a granular activated carbon in laboratory column systems. Sep Sci Technol 37–41:1039–1053

Gajjar P, Pettee B, Britt DW, Huang W, Johnson WP, Anderson AJ (2009) Antimicrobial activities of commercial nanoparticles against an environmental soil microbe, Pseudomonas putida KT2440. J Biol Eng 3:9. https://doi.org/10.1186/1754-1611-3-9

Ganesh R, Smeraldi J, Hosseini T, Khatib L, Olson BH, Rosso D (2010) Evaluation of nanocopper removal and toxicity in municipal wastewaters. Environ Sci Technol 44:7808–7813

Godinez IG, Darnault CJG (2011) Aggregation and transport of nanoTiO$_2$ in saturated porous media: effects of pH, surfactants and flow velocity. Water Res 45(2):839–851

Godinez IG, Darnault CJG, Khodadoust AP, Bogdan D (2013) Deposition and release kinetics of nanoTiO$_2$ in saturated porous media: effects of solution ionic strength and surfactants. Environ Pollut 174:106–113

Gong Y, Liu Y, Xiong Z, Kaback D, Zhao D (2012) Immobilization of mercury in field soil and sediment using carboxymethyl cellulose stabilized iron sulfide nanoparticles. Nanotechnology 23(29):1–7

Gong Y, Liu Y, Xiong Z, Zhao D (2014) Immobilization of mercury by carboxymethyl cellulose stabilized iron sulfide nanoparticles: reaction mechanisms and effects of stabilizer and water chemistry. Environ Sci Technol 48(7):3986–3994

Gottschalk F, Sondere T, Schols R, Nowack B (2009) Modeled environmental concentrations of engineered Nanomaterials for different regions. Environ Sci Technol 43(24):9216–9222

Guzman KAD, Finnegan MP, Banfield JF (2006) Influence of surface potential on aggregation and transport of titania nanoparticles. Environ Sci Technol 40(24):7688–7693

Han P, Wang X, Cai L, Tong M, Kim H (2014) Transport and retention behaviors of titanium dioxide nanoparticles in iron oxide-coated quartz sand: effects of pH, ionic strength, and humic acid. Colloids Surf A Physicochem Eng Asp 454(1):119–127

Han B, Zhang M, Zhao D, Feng Y (2015) Degradation of aqueous and soil-sorbed estradiol using a new class of stabilized manganese oxide nanoparticles. Water Res 70:288–299

He F, Zhao D (2007) Manipulating the size and dispersibility of zerovalent iron nanoparticles by use of carboxymethyl cellulose stabilizers. Environ Sci Technol 41(17):6216–6221

He F, Zhao DY, Liu JC, Roberts CB (2007) Stabilization of Fe–Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater. Ind Eng Chem Res 46(1):29–34

He F, Zhang M, Qian T, Zhao D (2009) Transport of carboxymethyl cellulose stabilized iron nanoparticles in porous media: column experiments and modeling. J Colloid Interface Sci 334 (1):96–102

He F, Zhao D, Paul C (2010) Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for in situ destruction of chlorinated solvents in source zones. Water Res 44 (7):2360–2370

Ho YS, McKay G (1998) The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. Can J Chem Eng 76(4):822–827

Hotze EM, Phenrat T, Lowry GV (2010) Nanoparticle aggregation: challenges to understanding transport and reactivity in the environment. J Environ Qual 39:1909–1924

Hou L, Li K, Ding Y, Li Y, Chen J, Wu X, Li X (2012) Removal of silver nanoparticles in simulated wastewater treatment processes and its impact on COD and NH$_4$ reduction. Chemosphere. Elsevier Ltd 87(3):248–252

Hydutsky BW, Mack EJ, Beckerman BB, Skluzacek JM, Mallouk TE (2007) Optimization of nano and microiron transport through sand columns using polyelectrolyte mixtures. Environ Sci Technol 41:6418–6424

Inyang M, Gao B, Wu L, Yao Y, Zhang M, Liu L (2013) Filtration of engineered nanoparticles in carbon-based fixed bed columns. Chem Eng J 220(2013):221–227

Jaisi DP, Saleh NB, Blake RE, Elimelech M (2008) Transport of single-walled carbon nanotubes in porous media: filtration mechanisms and reversibility. Environ Sci Technol 42:8317–8323

Jeong S-W, Kim SD (2009) Aggregation and transport of copper oxide nanoparticles in porous media. J Environ Monit 11(9):1595

Jiang X, Tong M, Kim H (2012) Influence of natural organic matter on the transport and deposition of zinc oxide nanoparticles in saturated porous media. J Colloid Interface. Sci Elsevier Inc. 386 (1):34–43

Johnson RP, Elimelech M (1995) Dynamics of colloid deposition in porous media: blocking based on random sequential adsorption. Langmuir 11:801–812

Johnson AC, Bowes MJ, Crossley A, Jarvie HP (2011) An assessment of the fate, behaviour and environmental risk associated with sunscreen TiO_2 nanoparticles in UK field scenarios. Sci Total Environ 409:2503–2501

Jones EH, Su C (2012) Fate and transport of elemental copper (Cu^0) nanoparticles through saturated porous media in the presence of organic materials. Water Res 46(7):2445–2456

Kanel SR, Goswami RR, Clement TP, Barnett MO, Zhao D (2008) Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media. Environ Sci Technol 42:896–900

Karn B, Kuiken T, Otto M (2009) Nanotechnology and in situ remediation: a review of the benefits and potential risks. Environ Health Perspect 117(12):1813–1831

Kasel D, Bradford SA, Simunek J, Outz T, Vereecken H, Klumpp E (2013) Limited transport of functionalized multi-walled carbon nanotubes` in two natural soils. Environ Pollut 180:152–158

Keller AA, Wang H, Zhou D, Lenihan HS, Cher G, Cardinale BJ, Miller R, Ji Z (2010) Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. Environ Sci Technol 44:1962–1967. https://doi.org/10.1021/es902987d

Khalid N, Mukri M, Mohamad K, Kamarudin F (2015) Influence of nanosoil particles in soft soil stabilization. Electron J Geotech Eng 20(2):731–738

Kirkegaard P, Hansen SF, Rygaard M (2015) Potential exposure and treatment efficiency of nanoparticles in water supplies based on wastewater reclamation. Environ Sci Nano 2:191–202

Kiser MA, Ryu H, Jang H, Hristovski K, Westerhoff P (2010) Biosorption of nanoparticles to heterotrophic wastewater biomass. Water Res. Elsevier Ltd 44(14):4105–4114

Limbach LK, Bereiter R, Muller E, Krebs R, Galli R, Stark WJ (2008) Removal of oxide nanoparticles in a model wastewater treatment plant: influence of agglomeration and surfactants on clearing efficiency. Environ Sci Technol 42(15):5828–5833

Liu R, Zhao D (2007) Reducing leachability and bioaccessibility of lead in soils using a new class of stabilized iron phosphate nanoparticles. Water Res 41(12):2491–2502

Liu X, O'Carroll DM, Petersen EJ, Qingguo H, Anderson CL (2009) Mobility of multiwalled carbon nanotubes in porous media. Environ Sci Technol 43(21):8153–8158

Liu HF, Qian TW, Zhao DY (2013) Reductive immobilization of perrhenate in soil and groundwater using starch-stabilized ZVI nanoparticles. Chin Sci Bull 58(2):275–281

Louie SM, Spielman-Sun ER, Small MJ, Tilton RD, Lowry GV (2015) Correlation of the physicochemical properties of natural organic matter samples from different sources to their effects on gold nanoparticle aggregation in monovalent electrolyte. Environ Sci Technol 49:2188–2198

Mashayekhi H, Ghosh S, Du P (2012) Effect of natural organic matter on aggregation behavior of C60 fullerene in water. J Colloid Interface Sci 374(1):111–117

Mueller NC, Nowack B (2008) Exposure modeling of engineered nanoparticles in the environment. Environ Sci Technol 42:4447–4453

Mylon SE, Chen KL, Elimelech M (2004) Influence of natural organic matter and ionic composition on the kinetics and structure of hematite colloid aggregation: implications to iron depletion in estuaries. Langmuir 20:9000–9006

Nohani E, Alimakan E (2015) The effect of nanoparticles on geotechnical properties of clay. Int J Life Sci 9(4):25–27

OECD Environment, Health and Safety Publications Series on Pollutant Release and Transfer Registers; No. 16 Global Pollutant Release and Transfer Register, Proposal for a Harmonized List of Pollutants. (2014)

Pan G, Li L, Zhao D, Chen H (2010) Immobilization of non-point phosphorus using stabilized magnetite nanoparticles with enhanced transportability and reactivity in soils. Environ Pollut 158(1):35–40

Pavlova-Verevkina OB, Ozerina LA, Politova ED, Surin NM, Ozerin AN (2009) Effect of electrolytesonthe slow aggregation of TiO2 nanocrystals. Colloid J 71(4):529–533

Pelley AJ, Tufenkji N (2008) Effect of particle size and natural organic matter on the migration of nano and microscale latex particles in saturated porous media. J Colloid Interface Sci 321:74–83

Pettibone JM, Cwiertny DM, Scherer M, Grassian VH (2008) Adsorption of organic acids on TiO_2 nanoparticles: effects of pH, nanoparticle size, and nanoparticle aggregation. Langmuir 24 (13):6659–6667

Phenrat T, Saleh N, Sirk K, Kim HJ, Tilton R, Lowry G (2008) Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. J Nanopart Res 10:795–814

Piplai T, Kumar A, Alappat BJ (2017) Removal of mixture of ZnO and CuO nanoparticles (NPs) from water using activated carbon in batch kinetic studies. Water Sci Technol 75(4):928–943

Piplai T, Kumar A, Alappat BJ (2018) Removal of ZnO and CuO nanoparticles (NPs) from water using activated carbon column. J Environ Eng 144(3):1–9

Qi Z, Zhang L, Chen W (2014) Transport of graphene oxide nanoparticles in saturated sandy soil. Environ Sci Processes Impacts 16(10):2268–2277

Ryan NJ, Elimelech M (1996) Review: colloid mobilization and transport in groundwater. Colloids Surf A Physicochem Eng Asp 107:1–56

Saleh N, Kim HJ, Phenrat T, Matyjaszewski K, Tilton RD, Lowry GV (2008) Ionic strength and composition affect the mobility of surface-modified Fe0 nanoparticles in water-saturated sand columns. Environ Sci Technol 42:3349–3355

Schrick B, Hydutsky BW, Blough JL, Mallouk TE (2004) Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. Chem Mater 16:2187–2193

Seetha N, Mohan Kumar MS, Hassanizadeh SM (2015a) Modeling the co-transport of viruses and colloids in unsaturated porous media. *J*. Contam Hydrol 181:82–101

Seetha N, Hassanizadeh SM, Mohan Kumar MS, Raoof A (2015b) Correlation equations for average deposition rate coefficients of nanoparticles in a cylindrical pore. Water Resour Res 51:8034–8059

Shani C, Weisbrod N, Yakirevich A (2008) Colloid transport through saturated sand columns: influence of physical and chemical surface properties on deposition. Colloids Surf A Physicochem Eng Asp 316(1–3):142–150

Solovitch N, Labille J, Rose J, Chaurand P, Borschneck D, Wiesner MR, Bottero JY (2010) Concurrent aggregation and deposition of TiO_2 nanoparticles in a sandy porous media. Environ Sci Technol 44(13):4897–4902

Syngouna VI, Chrysikopoulos CV (2013) Cotransport of clay colloids and viruses in water saturated porous media. Colloids Surf A Physicochem Eng Asp 416(2013):56–65

Syngouna VI, Chrysikopoulos CV (2015) Experimental investigation of virus and clay particles in partially saturated columns packed with glass beads. J Colloid Interface Sci 440:140–150

Taha MR, Taha OM (2012) Influence of Nanomaterial on the expansive and shrinkage soil behavior. J Nanopart Res 14:1–13. https://doi.org/10.1007/s11051-012-1190-0

Tan M, Qiu G, Ting Y (2015) Bioresource technology effects of ZnO nanoparticles on wastewater treatment and their removal behavior in a membrane bioreactor. Bioresour Technol 185:125–133

Torkzaban S, Bradford SA, van Genuchten MT, Walker SL (2008) Colloid transport in unsaturated porous media: the role of water content and ionic strength on particle straining. J Contam Hydrol 96(1–4):113–127

Tseng WJ, Lin KC (2003) Rheology and colloidal structure of aqueous TiO_2 nanoparticle suspensions. Mater Sci Eng A 355(1–2):186–192

Tumin ND, Chuah AL,Zawani Z, Rashid SA (2008) Adsorption of copper from aqueous solution by elais guineensis kernal activated carbon. J Eng Sci Technol 3(2):180–189, 33(6):587–590

Tungittiplakorn W, Lion LW, Cohen C, Kim JY (2004) Engineered polymeric nanoparticles for soil remediation. Environ Sci Technol 38(5):1605–1610

Walshe GE, Pang L, Flury M, Close ME, Flintoft M (2010) Effects of pH, ionic strength, dissolved organic matter, and flow rate on the co-transport of MS2 bacteriophages with kaolinite in gravel aquifer media. Water Res 44:1255–1269

Wan Yaacob WZ, Kamaruzaman N, Samsudin AR (2012) Development of Nanozero Valent Iron for the remediation of contaminated water. Chem Eng Trans 28:25–30. https://doi.org/10.3303/CET1228005

Wang C, Bobba AD, Attinti R, shen c, Lazouskaya V, Wang L-P, Jin Y (2012) Retention and transport of silica nanoparticles in saturated porous media: effect of concentration and particle size. Environ Sci Technol 46(13):7151–7158

Wang Z, Quik JT, Song L, van den Brandhof EJ, Wouterse M, Peijnenburg WJ (2015) Humic substances alleviate the aquatic toxicity of PVP-coated silver nanoparticles to organisms of different trophic levels. Environ Toxicol Chem 34:1239–1245

Waznea M, Liua X, Christodoulatosa C, Jasinkiewiczb KL (2008) Studies on boron nanoparticles aggregation and transport in porous media. J Colloid Interface Sci 330(1):90–96

Westerhoff P, Song G, Hristovski K, Kiser MA (2011) Occurrence and removal of titanium at full scale wastewater treatment plants: implications for TiO_2 nanomaterials. J Environ Monit 13 (5):1195–1203

Xiong Z, He F, Zhao D, Barnett MO (2009) Immobilization of mercury in sediment using stabilized iron sulfide nanoparticles. Water Res 43(20):5171–5179

Xu Y, Zhao D (2007) Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. Water Res 41(10):2101–2108

Yang GCC, Tu HC, Hung CH (2007) Stability of nanoiron slurries and their transport in the subsurface environment. Sep Purif Technol 58:166–172

Zhang G (2007) Soil nanoparticles and their influence on engineering properties of soils. In: Advances in measurement and modeling of soil behavior. https://doi.org/10.1061/40917(236)37

Zhang Y, Mi L, Wang PN, Ma J, Chen JY (2008) pH-dependent aggregation and photoluminescence behavior of thiol-capped CdTe quantum dots in aqueous solutions. J Lumin 128(12):1948–1951

Zhang W, Rattanaudompol US, Li H, Bouchard D (2013) Effects of humic and fulvic acids on aggregation of aqu/nC(60) nanoparticles. Water Res 47:1793–1802

Zhao LJ, Pirelta-Videa J, Hernandez-Viezcas J, Hong J, Gardea-Torresdey J (2012) Transport and retention behavior of ZnO nanoparticles in two natural soils: effect of surface coating and soil composition. J Nano Res 17:229–242

Zhou D, Keller AA (2010) Role of morphology in the aggregation kinetics of ZnO nanoparticles. Water Res 44:2948–2956

Zhu M, Wang H, Keller AA, Wang T, Li F (2014) The effect of humic acid on the aggregation of titanium dioxide nanoparticles under different pH and ionic strengths. Sci Total Environ 487:375–380

Chapter 5
Nanotechnology for Water Treatment

Zarshad Ali and Rashid Ahmad

Contents

5.1 Introduction 144
5.2 Wastewater Treatment 145
5.3 Carbon-Based Nano-adsorbents 146
  5.3.1 Organic Contaminant Removal 146
  5.3.2 Heavy Metal Removal 147
5.4 Antimicrobial Nanomaterials 147
  5.4.1 Chitosan and Peptides 147
  5.4.2 Silver Nanoparticles 148
  5.4.3 Titania Nanoparticles 148
  5.4.4 Zinc Oxide Nanoparticles 148
5.5 Polymeric Nano-adsorbents 149
  5.5.1 Dendrimer-Assisted Filtration 149
  5.5.2 Zeolites 150
  5.5.3 Cyclodextrins 151
  5.5.4 Fullerenes 152
  5.5.5 Functionalized Silica as Nano-adsorbent 153
5.6 Membranes and Membrane Processes 154
  5.6.1 Nanofiber Membranes 155
  5.6.2 Nanocomposite Membranes 156
  5.6.3 Thin-Film Nanocomposite Membranes 156
  5.6.4 Forward Osmosis 156
  5.6.5 Biological Membranes 157
5.7 Nanoparticles as Photocatalysts 158
  5.7.1 Nanophotocatalyst Optimization 158
5.8 Nanotechnology for Water Treatment: Pitfalls 161
5.9 Conclusions 162
References 163

Z. Ali
Department of Chemistry, Hazara University, Mansehra, Pakistan

R. Ahmad (✉)
Department of Chemistry, University of Malakand, Chakdara, Pakistan

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_5

Abstract Access to clean and cheap water resources is the global challenge and is one of the United Nation's Sustainable Developmental Goals. The problem is becoming overwhelming due to rapid increase in the world's population, global climatic changes, high-energy demands, and municipal and industrial contamination that threaten the reservoirs and sustainable supply of freshwater. Agricultural activities on the other hand are drawing more and more freshwater and continue to contaminate the freshwater reservoirs. These and other factors continue to press the need for technological advancement to safeguard against the scarcity of freshwater.

Modern-day water treatment technologies demand new approaches and improved materials for water resource conservation and management. Along with other long-range industrial applications, nanotechnology has the promise to ensure sustainable availability of clean drinking water and conservation of water resources through applying advance materials and techniques for water purification, conservation, and reuse. Current advancements in nanotechnology indicate that the many problems related to water quality can be successfully addressed by applying nanomaterials in the form of adsorbents, catalysts and catalytic membranes for enhanced filtration. The nanotechnology can be used in the key areas of water purification separations, bioremediation, and water disinfection with significant cost reduction and creating new economic opportunities for developing and underdeveloped countries. In this chapter, we review recent advancements in nanotechnologies for water purification, future direction and practical challenges in their commercialization and potential risks associated with nanoscale water remediation.

Keywords Nanotechnology · Bioremediation · Disinfection · Fullerene · Nanotubes · Nanosilver · Titania · Zinc oxide · Peptides · Chitosan · Bacteria · Virus · Membrane

5.1 Introduction

Supplying clean and affordable drinking water to the human population is the biggest challenge of the twenty-first century. The world's freshwater resources are continuously under stress due to rapid increase in population, climatic changes, intensive agriculture and industrial growth. Millions of people around the world have no access to clean and affordable drinking water and suffer from waterborne diseases (Devanathan 2017). Nanotechnology has a great potential to ensure provision of clean drinking water for the human population through increasing efficiency of wastewater and unconventional water resources. Nanotechnology has a wide-ranging application in various fields such as industries, storage technologies, optical and photonic applications, biotechnology and health care, but nowadays, nanomaterials and nanotechnology are extensively used as environmental cleanup strategies for the protection of environment through pollution control and wastewater treatment. Nanotechnology is used to purify contaminated water either by filtration or by separation techniques. Nanomaterials are extensively applied as separation media to remove organic and inorganic contaminants from water. The application of nanotechnology cannot only reduce the overall costs of water treatment on a large scale but can also reduce the cleanup time and level of contaminants to near-zero level in ecosystems.

5.2 Wastewater Treatment

Industrial operations require a large amount of water and thus produce large quantities of wastewater. The wastewater contains high concentrations of dissolved organic (dyes, etc.) and inorganic (heavy metals, etc.) contaminations. Traditionally, physical and chemical methods are used for the purification of industrial wastewater. These methods include precipitation, solvent extraction, ion exchange, ultrafiltration, reverse osmosis, flotation, coagulation, etc. All of them have their own merits and demerits. Most of these methods suffer from their inherent limitations such as low uptake of contaminants, high regeneration costs, low selectivities, and poor thermal, chemical, and mechanical stabilities. Filtration methods such as ultrafiltration, nanofiltration, and reverse osmosis are suitable alternatives to chemical separation. A major problem with filtration techniques is the disposal of concentrated sludge and regular cleanups and replacements are required which render them costly for the large-scale water treatment. To overcome the challenges of traditional wastewater treatment methods, modern-day technologies make use of more efficient methods for water purification. These techniques are based on nanocomposite membranes, polymeric adsorbents, and adsorption on nano-sized particles for the selective removal of the target contaminants present in industrial effluents and drinking water.

Nanoscale materials are very suitable for wastewater treatment and purification than their conventional counterparts due to their unique properties such as high surface area, high reactivity, greater opportunities for surface functionalization, and high selectivity for target contaminants. All these characteristics make them attractive candidates for their utility in adsorbents, catalysts, and sensors. Advancements in nanoscience and engineering offer immense opportunities to design new cost-efficient and eco-friendly water purification systems. Nanotech composite membranes, filters, and other materials can be regenerated and reused for a number of cycles, and thus the overall costs of water purification processes can be reduced. Figure 5.1 shows various technologies used for water desalination (Humplik et al. 2011). In this chapter, we present an overview of the various materials and techniques of nanotechnology for water remediation.

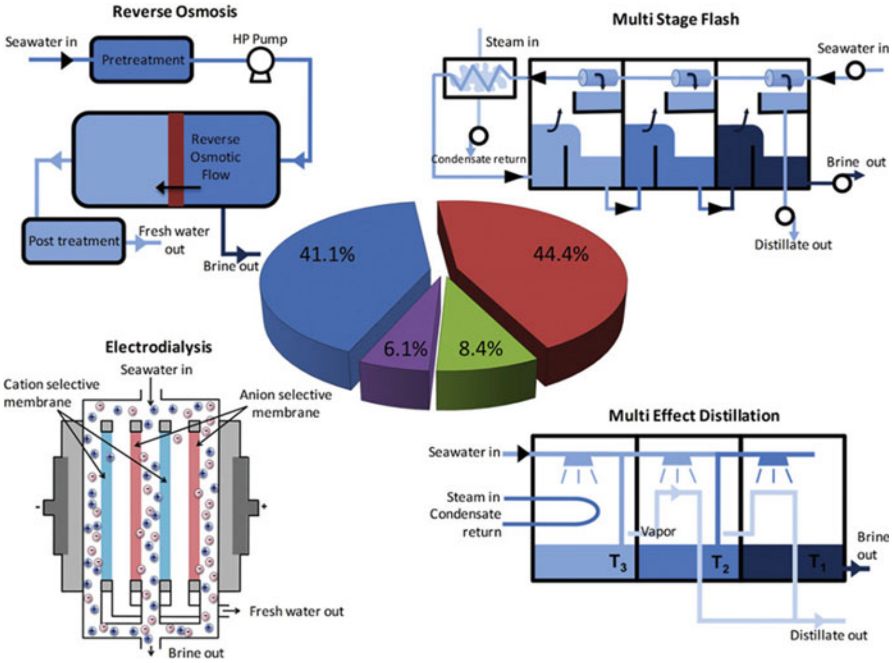


Fig. 5.1 Schematic diagram of major desalination technologies and their relative contributions to worldwide installed capacity for seawater and brackish water desalination. Multistage flash accounts for 44.4%, reverse osmosis 41.1%, multieffect distillation and thermal methods 8.4%, and electrodialysis and other methods 6.1%. (Adapted from Humplik et al. (2011), copyright © IOP Publishing. Reproduced with permission. All rights reserved)

5.3 Carbon-Based Nano-adsorbents

5.3.1 Organic Contaminant Removal

This class of nanomaterials consists of carbon nanotubes and activated carbons. Carbon nanotubes have high adsorption capacity than activated carbons (Yang and Xing 2010). The high adsorption capacity of carbon nanotubes originates from their large surface area and diverse interaction sites. Therefore, carbon nanotubes are more efficient adsorbent for the organic contaminants. Carbon nanotubes form loose aggregates due to their hydrophobic surface which contains interstitial channels that act as adsorption sites for organic molecules. On the other hand, activated carbons possess micropores which are inaccessible to bulky organic molecules such as antibiotics and pharmaceutical agents. Another disadvantage of the activated carbons is their lower affinity for small-sized polar organic molecules, while carbon nanotubes have much higher adsorption affinity for smaller organic molecules. This high reactivity of carbon nanotubes for organic molecules is due to their hydrophobicity, H-bonding, and covalent and electrostatic interactions with these molecules.

5.3.2 *Heavy Metal Removal*

The carbon nanotubes' surface possesfunctional groups like hydroxyl, phenol, and carboxyl that can electrostatically interact and make a chemical bond with heavy metal ions. Carbon nanotubes are therefore good adsorbents and offer fast kinetics for heavy metal ions removal. Carbon nanotubes are wide-spectrum adsorbents than activated carbons and have better adsorption capacities and fast kinetics for metal ions like lead, mercury, cadmium, etc. (Lu et al. 2006). The surface of the carbon nanotubes can be tuned by suitable functional groups for targeted removal/pre-concentration of contaminants for analytical applications.

5.4 Antimicrobial Nanomaterials

This class of nanomaterials consists of natural antibacterial agents, metals/oxides, and engineered nanoparticles. Various antimicrobial agents and their disinfection mechanisms are summarized as follows.

5.4.1 *Chitosan and Peptides*

The powerful oxidizing agents (chlorine, chloramines, and ozone) used nowadays as water disinfecting agents produce harmful by-products such as aldehydes, haloacetic acids, and trihalomethanes in drinking water. Some of them are carcinogenic and severely toxic for humans. Some alternate disinfection methods are required to avoid the use of harmful chemicals. The nanoparticles are supposed to be the suitable alternative for the chemical disinfection methods. They are relatively inert and also do not produce disinfection by-products in drinking water. Synthesized chitosan and peptides play a significant role in low-cost water decontamination systems. The antibacterial action of peptides is believed (Prathamesh 2011) to originate from the osmotic failure due to formation of microchannels in cell membranes. Various theories have proposed to explain the antimicrobial properties of chitosan nanoparticles. One mechanism proposed that chitosan nanoparticles enter into the cell membrane and bind with deoxyribonucleic acid (DNA) and thus hinder ribonucleic acid (RNA) synthesis. Chitosan and peptides are used in surface coating of water tanks or as antimicrobial agents in membrane applications.

5.4.2 Silver Nanoparticles

Silver and its compounds are historically known to exhibit antimicrobial abilities and are used in disinfection and water treatment applications. Silver nanoparticles are known to have a wide range of antimicrobial activity. The antimicrobial activity of the silver nanoparticles stems from their chemical affinity for sulfur and phosphorus which is key for their biological activities. Silver nanoparticles release a large amount of free silver ions (Ag^+) that can bind to the thiol groups of enzymes and protein and make them inactive. Silver ions also prevent DNA and RNA replication and damage them. Silver nanoparticles display photocatalytic activity in the presence of ultraviolet light and are therefore useful antimicrobial agents. Nanoparticles of silver in zerovalent state have been shown to have antimicrobial and antiviral activities and are promising material for application in water purification plants. Currently, a number of water treatment technologies use silver nanoparticle-impregnated membrane for water purification. Some devices using silver nanoparticles are already available in the market, e.g., aqua pure and marathon systems. Silver nanoparticles are also employed in ceramic microfilter for pathogen disinfections.

5.4.3 Titania Nanoparticles

Titania nanoparticles show excellent antimicrobial activity and are widely applied in disinfection applications nowadays. Titanium dioxide nanoparticles are easily available, are low cost, and have low toxicity (Liu et al. 2017) and show excellent photocatalytic activity in the presence of ultraviolet (UV) or sunlight. The antibacterial activity is due to the production of peroxides and hydroxyl free radicals in the cell under UV light. The antimicrobial activity of titanium dioxide can be enhanced by doping with other metals. These nanoparticles can also be used as membrane filter, suspension, or coating on the UV reactor surface.

5.4.4 Zinc Oxide Nanoparticles

Zinc oxide nanoparticles act as strong antibacterial agents against a wide range of bacteria. Like titania, zinc oxide nanoparticles continue to be explored for the removal of organic contaminants from drinking water samples. The antibacterial action of zinc oxide nanoparticle is not yet well established, but it is believed that the photocatalytic activity of zinc oxide nanoparticles arises from the production of hydrogen peroxide which oxidizes the cell components. Another mechanism suggests that these nanoparticles enter into the cell, disorganize the cell membrane, and thus inhibit bacterial growth. Some researchers have used zinc oxide nanoparticles

Table 5.1 Nanotechnological applications using antimicrobial nanomaterials

Nanomaterial	Antimicrobial mechanism	Current applications	Potential future applications
Silver	Discharge of Ag^+ ions, damage DNA, disrupt cell membrane and electron transport	Used in water filters, medical devices, and coating in washing machine, refrigerators, and food containers	Membranes and surface coatings
Zinc oxide	Cause destruction in cell membrane, produce hydrogen peroxide, and discharge Zn+ ions	Used in antibacterial cream, self-cleaningglass, lotions, ointment, and ceramics	
Titania	Produce reactive oxygen species and damage cell wall and cell membrane	Used for organic pollutant degradation, in air purifier and water purification systems	UV disinfection of waste water, biofouling-resistant surfaces, and reactive membranes
Carbon nanotubes	Physically compromise cell envelope	None	Biofouling-resistant membranes, carbon hollow fiber, filter, etc.
Chitosan	Destroy the structure of membrane	Used in personal care products, biomedical products, and wastewater treatment	Immobilizer of bacteria, enzymes, and other biological molecules/ biosorbents

for sensing and photocatalytic degradation of chlorinated phenols (Ba-Abbad et al. 2017). Researchers are also interested to modify the surface of nanoparticles with organic/inorganic dyes for their photochemical applications in visible light for the degradation of environmental pollutants. Zinc oxide nanoparticles are considered harmful to aquatic life and their use in drinking water treatment is limited. Nanomaterials used as antimicrobial agents for various technological applications are summarized in Table 5.1.

5.5 Polymeric Nano-adsorbents

5.5.1 *Dendrimer-Assisted Filtration*

Dendrimers are tailor-made adsorbents which are used for the removal of heavy metals and organic contaminants. They are highly advanced materials that can remove both heavy metals and organic pollutants in a single-step process. The interior hydrophobic part of the dendrimers can adsorb the organic, while the exterior branches are functionalized with organic functional groups such as amines and hydroxyl for trapping toxic heavy metals (Ali et al. 2015). The sorption mechanisms for dendrimer-enhanced filtration are usually complexation, electrostatic attraction, and H-bonding. Some researchers (Sajid and Nazal 2017) have

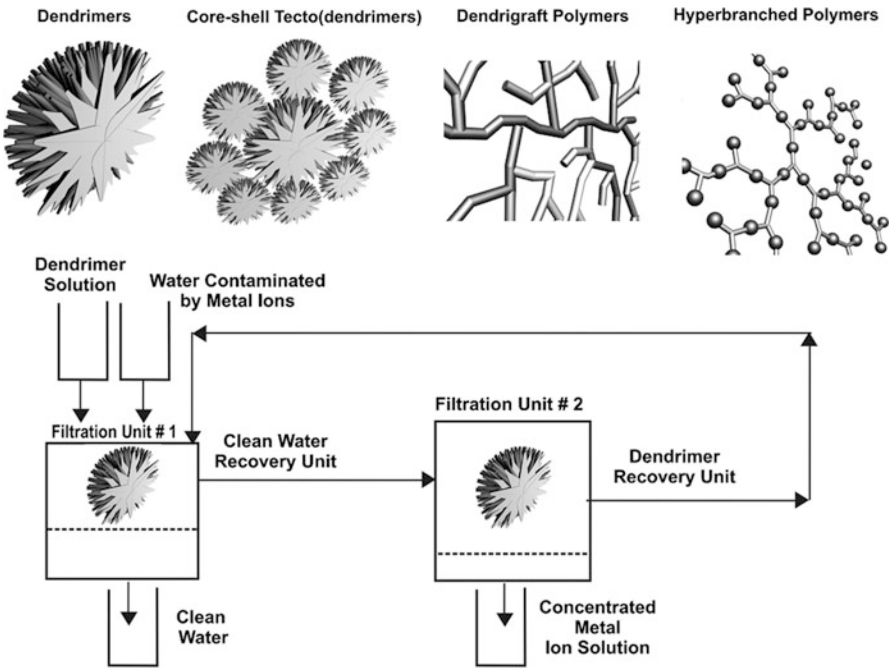


Fig. 5.2 Dendrimer-enhanced filtration. (Adapted from Theron et al. 2008, copyright© Taylor & Francis LTD, www.tandfonline.com)

designed dendrimer-based ultrafiltration assembly that was successfully used for the removal of metal ions and organic pollutants from water. In addition, highly efficient chitosan-based nano-adsorbents have also been effectively used for the removal of anionic dyes from textile wastewaters. The nano-adsorbent was biodegradable and was nontoxic, which achieved almost complete removal of textile dye. Operation complexity and multistage cost-intensive dendrimer synthesis are the key restrictions in their commercial-scale applications; however, their commercial entry is ongoing, and some companies in China commercially supply polymer-based filtration devices. A typical dendrimer-based filtration assembly is sketched in Fig. 5.2 (Theron et al. 2008).

5.5.2 Zeolites

Zeolites are ordered microporous aluminosilicate molecular sieves with a pore size of about 3–8 °A. Zeolites are either naturally occurring or synthesized at high temperature. The size of zeolites can be controlled to a few nanometers or centimeters by varying synthesis conditions. Zeolites are highly porous materials, and their porosity varies among different zeolite families and is generally in the range of

30–40%. The high porosity of zeolites in addition to high surface area has led to their application in separation and catalysis. The most common commercial use of zeolite is as an adsorbent during various chemical processes. High mechanical/chemical stability and high surface area make them particularly interesting for water purification and ion exchange. The type of embedded cation, size, charge, and the extent of exposure have great effect on their adsorption properties and selectivity. Zeolites having higher Si contents are hydrophobic in nature and have high affinity for phenol adsorption (Wiesner and Bottero 2007). Thin-film nanocomposite membranes having nanozeolites in their polyamide layer possess enhanced permeability for water molecules and block hydrated ions due to their hydrophobic nature. The Ag^+ ions embedded in zeolites can also act as antimicrobial agents, where the Ag^+ ions are released through ion exchange. When used for water remediation, the Ag^+ attacks the microorganism and inhibits their production; a similar disinfection mechanism is reflected in the operation of Agion® (Sciessent LLC, Wakefield, MA, USA). When placed in water, a small amount of silver is released which acts as a disinfection medium. Such nanocomposite membranes are in the early stage of marketing. Some natural zeolites, for example, clinoptilolite and chabazite, are used for the removal of radionuclide such as ^{90}Sr and ^{137}Cs from radioactive wastewater. Zeolites are also used for the cleaning of radionuclear wastes produced from nuclear power station crash. Zeolites are effective in the elimination of toxic heavy metals from ground- and runoff waters, whereas clinoptilolite is very selective for removing ammonium ion (NH_4^+) from wastewater. On the other hand, surface-modified zeolites have shown higher efficiency for humic acid and nitrate adsorption than commercially available zeolites. Nanometric-sized zeolites have also been synthesized to selectively oxidize toluene to benzaldehyde (Jesudoss et al. 2018). This oxidation is more environmentally friendly with minimum energy requirement, and no harmful secondary photochemical reactions occur.

5.5.3 *Cyclodextrins*

Cyclodextrins are cyclic oligosaccharide polymeric particles having well-defined cylindrical holes for the entrapment of organic pollutants. Cyclodextrins are homogeneous crystalline substances having glucopyranose rings. These rings are made of 6, 7, and 8 glucopyranose units. Cyclodextrin polymers are obtained in the form of powders, granules, and thin films for use in different devices and water treatment applications. Cyclodextrins are not only used for water treatment but are also used for the removal of organic contaminants and cleaning of oil. Cyclodextrins have a remarkable ability of forming inclusion complexes with liquids, solids, and other gaseous molecules through chemical complexation. During this chemical complexation reaction, other guest solid, liquid, and gaseous molecules are entrapped within the pores and cavities of the cyclodextrins. The researchers have shown that cyclodextrins can remove a wide range of organic pollutants such as fertilizers, explosives, pesticides, acetones, fluorines, and polyaromatic hydrocarbons. These reports have shown that cyclodextrins have better performance than zeolites and activated carbons and can reduce these organic contaminants in water to parts per trillions, while activated carbons and zeolites can reduce them to only parts per million level in water (Amit et al. 2011). In addition to better cleaning performance, cyclodextrins have strong bonding interactions with organic pollutants than activated carbons. Cyclodextrins are nonhygroscopic in nature and are not deactivated and deteriorated by the absorption of water and can be effectively used in humid conditions. They can form a very strong bond with the pollutants and are not leached once they are adsorbed on the surface. Cyclodextrins have adsorption capacities of 22 mg of organic contaminants per gram of the cyclodextrin polymer in comparison with 58 mg/g of activated carbons. Cyclodextrin polymer is cheaper and can be reused several times without any significant decrease in the adsorption capabilities. Cyclodextrins can be easily regenerated by using alcohols such as ethanol and methanol. In addition to these advantages, cyclodextrin can also be packed in columns and bed filters for the treatment of water, and granular cyclodextrin can be directly poured into the water and can also be used in the form of membrane. Different physical forms of cyclodextrins allow the flexibility of design for water treatment applications and can be used in water filters, in membranes, and as adsorbent. Cyclodextrins have been shown to remove highly toxic cyanobacteria from drinking water and agro-compounds such as para-nitrophenol and methyl chloride and have been compared with activated carbons and mesoporous silica. Chemically conjugated beta-cyclodextrins have been shown to remove azo dyes such as Evans blue and Chicago sky blue and aromatic amines from water. Further, cyclodextrins and their derivatives can also remove pesticides, polyaromatic hydrocarbons, methane, ethers, and esters. In addition to these, cyclodextrin-impregnated ceramic filters have been effectively used for the purification of water and removal of environmental contaminants. Cyclodextrin derivatives have also been used for the removal of metals such as lead and mercury from soil.

5.5.4 Fullerenes

Fullerene is a special class of compounds entirely composed of carbon atoms. The first representative of this class is buckminsterfullerene which was discovered in 1985 and contains 60 carbons, forming a hollow spherical cage. Currently fullerenes are not used in water treatment but have potential applicability. Like fullerol or hydroxylated fullerene, comparatively C_{60} is nontoxic and is believed to possess photocatalytic activity and can be used for water disinfection or photochemical degradation of contaminants. Carbon nanotubes are another class of fullerene and have been reported to have antimicrobial properties. Carbon nanotubes have been discussed in detail in Sect. 5.6.5 of this chapter. The antimicrobial ability of this class of compounds is due to the production of reactive oxygenated species which ruptures the DNA of the bacterial cell and inactivates virus. The antimicrobial ability of nanoparticle can overcome the problems associated with traditional chemical disinfections of chlorine and ozone. These nanoparticles can overcome the problems of production of harmful by-products and short-term reactivity associated with chemical disinfection. The reactive oxygenated species produced by fullerene could be utilized for the production of oxidizing species to degrade organic pollutants in water. The ability of fullerene to rupture DNA and inactivate virus could be effectively used for water disinfection. Fabricating the fullerene-based membrane can overcome the problem of biofouling of the membrane frequently encountered in membrane filters. The derivative of fullerene can be potentially used in photocatalytic water treatment such as amino fullerene which can produce singlet oxygen species ($^1O_2$) on exposure to visible light having wavelength less than 550 nm. Amino fullerene under visible light irradiation has been used to study the degradation of pharmaceutical compounds and inactivate viruses. The fullerenes are more expensive and are not as radially available as other nanoparticles, and their application for water treatment is still in research stage.

5.5.5 Functionalized Silica as Nano-adsorbent

They are functionalized ceramic materials with hexagonal nanoporous structures. Silica is the polymeric form of silicic acid that consists of repeated SiO_4 units arranged tetrahedrally. Ordinary silica is synthesized from silicon tetrachloride, orthosilicates, or sodium silicates. Silica aerogels have gained widespread popularity and attention of researchers since their discovery in 1992 (Mobil research group). Silica possesses high surface area, low density, high mechanical, chemical, and thermal resistance that led to their widespread practical applications in catalysis and separation. Silica has a highly porous three-dimensional structure which is accessible to the sorbed molecules. The traditional harsh processing conditions for the synthesis of silica make it inconvenient to incorporate temperature-sensitive organic molecules during the synthesis of organic-inorganic hybrids. Therefore, sol-gel process is widely used for the synthesis of highly porous silica glasses. The sol-gel silica, due to operation simplicity, allows the incorporation of temperature-sensitive dopants into the silica matrix for the synthesis of hybrid silica and has universal technical and commercial importance. Suitable organic functional groups can be grafted on the surface of silica, which allow this class of materials to bind a wide range of organic contaminants and heavy metals in case of ground- and wastewater remediation. Generally, three steps are involved in the synthesis of silica such as (1) preparation of highly ordered liquid crystalline micelle template, (2) oxide precipitation on micelle surface, and (3) calcination of oxides to remove organic template and addition of silanes to form a monolayer. In their specific application for the waster/wastewater treatment, these functionalized silicas are dispersed in the polluted water, where they bind the contaminants by electrostatic interaction or through formation of a chemical bond. The dispersed nanosilica adsorbent can be recovered by filtration and recycled after the removal of target contaminants. Functionalized nanomaterials such as metal oxides, carbon nanotubes, dendrimers, and zeolites are shown in Fig. 5.3 (Savage and Diallo 2005).

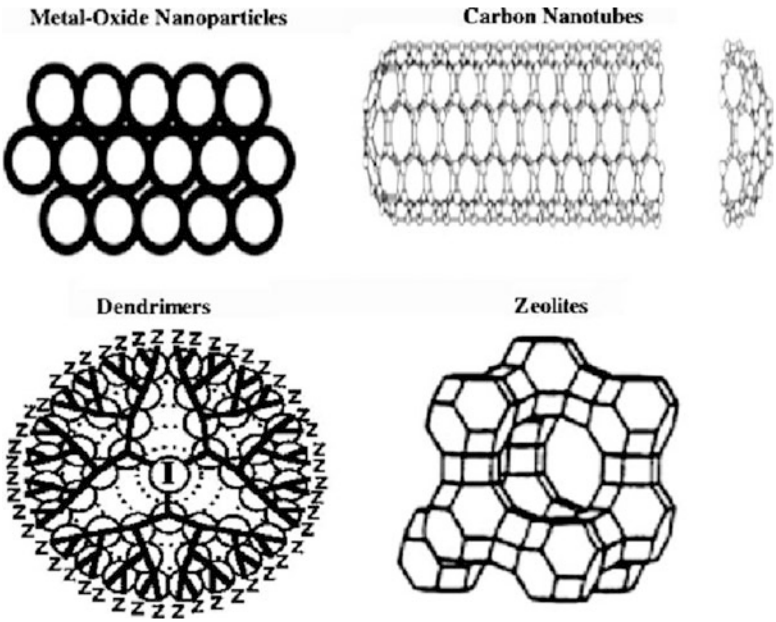


Fig. 5.3 Functional nanomaterials evaluated for water purification. (Adapted from Savage and Diallo 2005), copyright © 2005, Springer Nature)

5.6 Membranes and Membrane Processes

The use of membranes and membrane system for water purification and desalination is growing rapidly. Their function is to create a physical barrier for the contaminants. These membranes are characterized by their repeated use, full automation, and less chemicals and allow flexible design. But the major problems of membrane fouling such as organic and biofouling are the barriers in their applications for wastewater treatment. High-energy requirements due to membrane fouling is another barrier in the widespread applications of pressure-driven membrane processes. Modern-day water treatment technologies aim at the removal of toxic constituents from water, but the diversity of these undesired constituents and their properties demand multistage operations. The introduction of photocatalytic materials avoids fouling but makes the membrane "reactive" instead of creating a characteristic "physical barrier" that can achieve multiple treatment goals in one reactor. The efficiency and performance of the membrane is usually decided by the membrane material. Introduction of functional materials into membranes improves their permeability and thermal/ mechanical stability and increases their resistance to fouling. These functional materials are also helpful in pollutant degradation and self-cleaning of the membranes.

5.6.1 Nanofiber Membranes

Nanofibers are produced by electrospinning of different materials like polymers or ceramics in an electric field (Fig. 5.4) (Ahmed et al. 2013). The nanofibers have high surface area, high porosity, and complex pore structure. The various properties of nanofiber such as chemical composition, morphology, and diameter and the spatial arrangement of electrospun fiber can be tuned for the specific applications accordingly. They are used as a pretreatment procedure before reverse osmosis. Nanofibrous membranes have been utilized commercially for air filtration but have not been applied for water purification yet. These membranes can clean micro-sized particles from aqueous solutions and have significant resistance to fouling. Additionally, organic functional groups can be also incorporated in nanofibers during electrospinning of solution to synthesize affinity membrane for water treatment and desalination (Cloete et al. 2010). Such polysulfonate-functionalized membrane is able to decompose organic pollutants such as nitrophenols and can selectively bind metal ions. Similarly, silver-doped nanoparticle membranes have also shown great promise for binding some bacteria such as *E. coli* and *P. mendocina* and were also effective in virus removal. Such membranes also offer resistance to biofouling because the Ag^+ ions prohibit the attachment of bacteria to the membrane surface. An electropositive nanofiber filter called NanoCeram is already patented (Argonide Corporation, Sanford, USA). NanoCeram has a high surface area and is produced in large quantity by sol-gel reaction. Such membrane can capture bacteria, virus, and protein through an electrostatic effect.

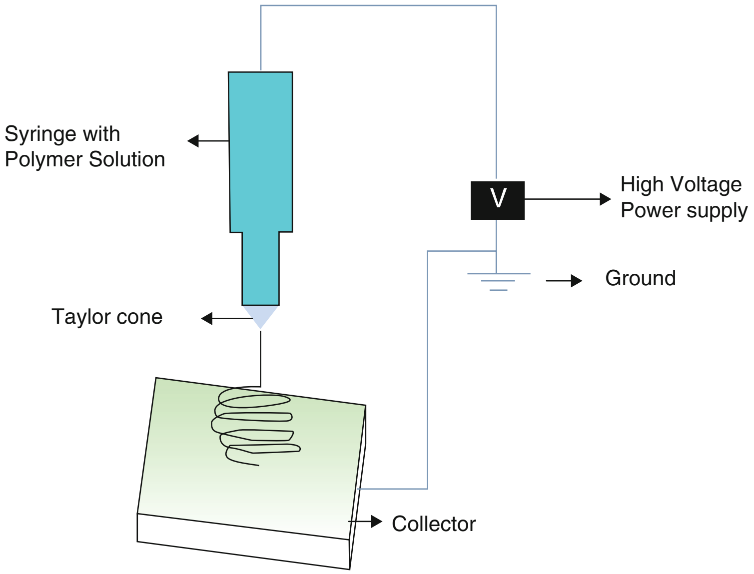


Fig. 5.4 Electrospinning technique for modification of nanofiber membrane. (Adapted from Ahmad et al. 2013)

5.6.2 Nanocomposite Membranes

One of the research objectives of nanotechnology-induced water filtration is to reduce membrane biofouling. For this purpose, a number of studies have been devoted to incorporate nanomaterials into polymeric and inorganic membranes. Nanoparticle oxides such as silica, alumina/titania (Al_2O_3, TiO_2), and zeolites have been used for this purpose. Besides, nanoparticles with antimicrobial actions such as nanosilver, carbon nanotubes, and photocatalytic nanomaterials such as titania have been incorporated into membrane systems. These inorganic nanomaterials increase resistance to fouling, enhance mechanical and thermal stability, and reduce thermal permeability of the polymeric membranes. Nanosilver-grafted polymeric membranes have increased biofouling resistance due to bacterial inhibition and viral inactivation, but the long-term resistance to biofouling is still a problem which needs to be addressed for their effective and long-term applications in water treatment technologies. Photocatalytic nanoparticle-incorporated membranes utilize the advantages of physical separation of the membrane as well as the chemical reactivity of nanoparticles for organic contaminant degradation such as chlorinated compounds.

5.6.3 Thin-Film Nanocomposite Membranes

Thin-film nanocomposite membranes are synthesized by doping or casting nanomaterials into the active layers of thin films. The nanomaterials usually incorporated in thin films are nanosilver, titania, and zeolites. The performance of these membranes depends on the type and amount of nanomaterials involved. Nanozeolite is the most frequently used material in such applications. Various studies have shown that the incorporation of zeolite leads to enhanced permeability of the membrane and the development of negative charge on the membrane surface. Nano-sized zeolite also acts as a carrier for antimicrobial agents such as Ag^+ and increases antifouling ability of the membrane. Zeolite-based thin-film nanocomposite membrane technology has achieved the early stage of commercialization and quantum flux (NanoH_2O, Los Angeles, CA, USA); seawater treatment membrane is available in the market.

5.6.4 Forward Osmosis

Forward osmosis is a membrane technique which makes use of osmotic gradient and draws water from low osmotic pressure to high osmotic pressure solution. The draw solution is then treated thermally, or by reverse osmosis, to produce pure water. Forward osmosis does not require high pressure and makes the membrane less susceptible to fouling than ordinary pressure-driven reverse osmosis. Some chemicals like sodium chloride (NaCl) and ammonium bicarbonate (NH_4HCO_3) are employed currently for generating draw solutions. Both thermal process and reverse osmosis are energy demanding for recovering water from the draw solutions. To reduce the energy consumption, magnetic nanoparticles are developed recently as a new type of solute for draw solution owing to their easy separation and reuse. Instead, hydrophilic coating was also utilized to increase dissolution and osmotic pressure. For example, forward osmosis generated a fluid flux greater than 10 L/ m^2 h^{-1}, when polyethylene glycol-coated magnetic nanoparticles were used as coating and deionized water as feed solution. Recently, magnetic nanoparticles ($Fe_3O_4@SiO_2$) were also used for recovering $Al_2 (SO_4)_3$ by flocculation.

5.6.5 Biological Membranes

These membranes are protein based and also known as "aquaporin-based membranes." Aquaporin is universally present in living cells and forms selective channels under certain conditions, which block undesired ionic molecules. High selectivity and water permeability make them promising candidates for water treatment applications. A major disadvantage of these materials is that they are too weak and cannot stand alone; therefore, they are always used as vesicles and supported on polymeric membrane for practical applications. The first commercial biologically inspired membrane is "Aquaporin Inside™" marketed by Aquaporin A/S, Copenhagen, Denmark. This membrane meets all the requirements for brackish water desalination and can withstand pressures up to 10 bar and allow a water flux more than 100 L/ hm^2.

Aligned carbon nanotubes also possess smooth nano-sized channels and have been shown theoretically to provide faster water permeation. It was also predicted that the membrane containing only 0.03% of aligned carbon nanotubes can provide a flux greater than the available commercial membranes used for seawater desalination (Pendergast and Hoek 2011). However, due to uneven pore diameter in aligned carbon nanotubes, salt and small-sized molecules' high rejection is still a challenge. It was proposed that grafting functional groups at nanotube gating can improve the selectivity of aligned carbon nanotube membrane (Yang et al. 2013). For example, grafting carboxyl groups on carbon nanotube openings, 98% rejection of $Fe(CN_6)^{-3}$ was achieved at low ionic strength; however, KCl rejection was decreased by increasing ionic strength. Grafting of bulky groups at nanotube openings can physically eliminate salts, but membrane permeability will be significantly decreased due to stearic hindrance. Currently, aligned carbon nanotube membranes are not applicable for water desalination; however, for effective desalination, the carbon nanotube diameter should be uniformly less than 0.8 nm. Membrane fabrication and large-scale production of carbon nanotubes are the key challenges in the commercial implementation of both aligned carbon nanotubes and aquaporin-based membranes, especially scale-up production, and purification of aquaporin is a challenge. Chemical vapor deposition technique is most commonly used for production of aligned carbon nanotubes, which paved a way for their commercial application. Various nanomaterials-based technologies for current water desalination applications are summarized in Table 5.2.

5.7 Nanoparticles as Photocatalysts

Nanoparticles have large surface area, small size, and excellent optical and electronic properties. These characteristics make these nanostructured particles promising materials to act as water remediation catalysts. Photocatalysis is an advance oxidation process for the elimination of low-level pollutants and microorganism. This process is usually used for the treatment of hazardous nonbiodegradable contaminants. Slow kinetics due to limited light availability is the main disadvantage of this process, and nowadays research is mainly focused on how to overcome these difficulties.

5.7.1 Nanophotocatalyst Optimization

Titania is chemically stable, less toxic, low cost, and abundant and is widely reported as photocatalyst for water and wastewater remediation. During the last decade, titania has emerged as a semiconductor photocatalyst, which acts as oxidative-reductive media for organic and inorganic contaminants. When exposed to UV light, the electrons are excited to the conduction band, and as a result electron/hole pairs (e^- +/h^+) are generated. These electron/hole pairs start complex chain oxidation-reduction reactions and as a result lead to the formation of reactive oxygen species at the surface or undergo unwanted recombination. Mechanistically, the possible traps for these electron holes are water and hydroxyl ions, which result in the formation of hydroxyl (OH•) radicals. These hydroxyl radicals are strong oxidizing agents. The electron trap adsorbs oxygen, and an unstable superoxide ($O•_2$) species is produced. These oxygen-rich reactive species (OH•, O_2•) react with the adsorbed molecules on the photocatalytic surface and carbon dioxide, and water is produced after complex oxidation and hydroxylation reactions (Dasgupta et al. 2017). Electron/hole pair production can be reduced by optimizing shape/size of titania, noble metal doping, and surface treatment, and the photocatalytic efficiency can be improved by enhancing surface adsorption. The size of titania is the key parameter and controls solid-phase transformation, adsorption, and electron/hole (e^-/h^+) dynamics. Rutile, the crystalline form of titania, is stable for particle size larger than 35 nm, while anatase is stable for particle size less than 11 nm and is efficient for reactive oxygenated species production. The slow kinetics of titania photocatalyst is because of the recombination of electron (e^-) and its hole (h^+), and by decreasing the particle size, the recombination can be decreased and catalytic efficiency can be improved. However, by further decreasing the particle size to several nanometers, the photocatalytic efficiency decreases due to increase in surface recombination. In comparison to titania, titania nanotubes are more efficient photocatalysts for the decomposition of organic compounds. The higher photocatalytic efficiency of titania nanotubes is attributed to their fast mass transfer kinetics and shorter carrier diffusion path in the walls of nanotubes. The ultraviolet light comprises only 5% of the electromagnetic spectrum which is therefore a key drawback in the commercial-scale application of titania nanophotocatalyst. Photocatalytic activation of titania is usually achieved by ultraviolet lamp, but sunlight can also be used for this purpose in addition to artificial source. For

Table 5.2 Nanotechnology applications for wastewater treatment

Nanofiltration-based technology	Properties	Current applications	Advantages
Dendrimer-enhanced filtration	The polyamidoamine and polypropylene imine are easier to filter due to their spherical structure and larger size	Removal of wastewater cations, anions, and organic compounds and the inactivation of bacteria and virus. Used as a stabilizer	Metal nanoparticles and long-chain aliphatic can be activated on dendrimer surfaces without affecting the binding properties of organic species
Carbon nanotube membranes	Man-sized rolled-up graphene sheets with cylindrical structure, high surface areas, permeability, and excellent mechanical and thermal stabilities	They have the ability to remove a wide range of water contaminants such as bacteria, viruses, and other organic pollutants	Due to their smooth interior, carbon nanotubes can perform faster than other membranes. Cost-effective, durable, and can be reused
Nanoscale titania photocatalysts	Nanoscale titania can function both as a photocatalyst and as an adsorbent	Nanoscale titania can break down nearly all organic pollutants and absorb biological contaminants and heavy metals	Nanoscale titania has large surface area and faster photocatalytic abilities than larger titania particles
Zeolites	Zeolites are porous crystalline adsorptive materials made from silicon-aluminum solutions like fly ash	Generally used for the treatment of heavy metals like lead and mercury and bacteria and as ion exchange media in column filtration	Zeolite-Ag compounds have been found effective against bacteria and molds. They are produced cheaply because of abundant and naturally available sources
Functionalized silica as nano-adsorbent	Functionalized silicas are tailored glass or ceramic materials with attached organic moieties. They are microporous and selective for contaminants	Removal of metals from water, ion exchange, and catalysis	They have faster adsorption kinetics, higher adsorption capacity, and superior selectivity

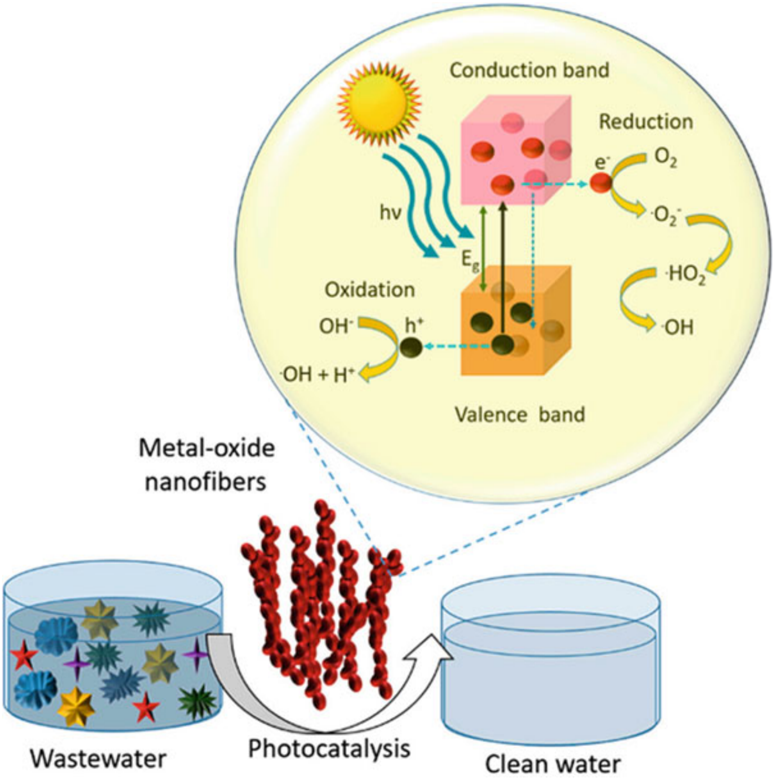


Fig. 5.5 Illustration of the metal oxide nanofiber-mediated photocatalysis. (Adapted from Mondal 2017)

example, KRONO Clean 7000 (Kronos Inc., Cranbury, NJ, USA) is a photocatalyst, where the bandgap is relatively of lower energy and it can make use of the broader portion of the electromagnetic spectrum. In addition to titania, tungsten dioxide, some derivatives of fullerene, and poly(N-vinylpyrrolidone)-encapsulated C_{60} have a better photocatalytic activity under visible light irradiations. However, these materials produce $^1O_2$ which has lower oxidation potential, and their prices are relatively high. Various approaches to enhance the photocatalytic efficiency of titania include creation of efficient titania nanotubes, noble metal doping, and lowering e−/h + recombinations. A schematic representation of metal oxide-based catalysis is given in Fig. 5.5 (Mondal 2017).

Titania-based nanophotocatalysts have been effectively used for the removal of organic and inorganic contaminants from water. These photocatalysts can degrade chlorinated benzenes and alkanes, furans, and polychlorinated biphenyls and can also reduce toxic heavy metal ions such as chromium and silver platinum under the action of UV light. Apart from this, light-activated titania nanoparticles have gained significant attention, and some researchers have reported (Safardoust-Hojaghan and Salavati-Niasari 2017) photochemical degradation of methylene blue under the action of visible light and photocatalytic degradation of dichloroacetic acid and carbon tetrachloride in aqueous solution by titania nanocomposites (Ribao et al. 2017). Advance oxidation process of water treatment technology is already in the market, for example, Purific Water (Holiday, Florida, USA) is a water purification system which makes use of the combined processes of photocatalysis and ceramic membrane filtration. This assembly has a capacity of more than four million cubic meter per day and can also degrade organic compounds.

5.8 Nanotechnology for Water Treatment: Pitfalls

Nanotechnology is the greatest scientific venture of the twenty-first century, which revolutionized many fields of science and technology such as consumer goods, manufacturing methods, and material engineering particularly in addition to water and wastewater treatment. The overwhelming benefits of nanotechnology dominated the scientific mass media coverage, and the adverse effects of using nanotechnology remained masked. Only recently, the environmental safety concerns about nanotechnology have been discussed in media. Potential risks may arise from the nature of the nanoparticles themselves. The high specific surface area, crystalline structure, and reactivity which are the key benefits of nanoparticles may facilitate the transport of man-sized materials in the environment and their reactivity with the cellular materials and may cause biological harms. We already know that computer chips contain toxic gallium arsenide, and millions of cellular phones and computers are disposed every year. What is the environmental fate of these materials? The nanotechnology may not be totally environment friendly. The environmental scientists and other regulation authorities should asses the harmful effects of nanotechnology, and we must answer a few questions raised about nanotechnology urgently. For example, nanoparticles can self-assemble in an assembly. Can they replicate in the environment? What are the health impacts and the fate of these nanoparticles in the environment? Can these nanoparticles be recovered for reuse or will these nanoparticles decompose into environment-friendly end products? It is therefore imperative to assess the usefulness and outcome of the current water treatment technologies in terms of pollution and other harmful effects.

Currently, no standard method exists which could readily monitor and detect nanoscale materials in the environment. The existing analytical technique for quantifying nanomaterials is time consuming and demands costly instruments and expertise. Lack of regulatory requirement, critical data, and information about the occurrence and fate of these materials makes this task further complicated. The researchers are required to develop water treatment technologies keeping in mind the possible environmental impact of these materials by using environment-friendly precursors, synthesis, and designs. The bioavailability and ecotoxicity of these nanoscale materials are currently unknown. Nanotechnology is an interdisciplinary science and can pose further challenges for environmental specialists and engineers. We must be aware of the possible amplifications of these materials that they can enter the food chain and can be transported by water.

5.9 Conclusions

Recent interests in the application of nanotechnology for water purification are driven by its high efficiency, low cost, selective removal of the contaminants, and durability. The researchers believe that the future nanotechnology will benefit from the properties of nanomaterials. Nanotechnology cannot only reduce the overall costs of the water treatment but also the time of cleanup operations and the concentration of some of the contaminants to near-zero level. Some of the nanotechnology-based water purification devices are already in the market, while some others are in the research stage. In the future, advancements in nanotechnology are likely to fulfill the current requirements of water treatment through the use of improved nanomaterials in membrane filters, adsorption, ion exchange, resins, and other sorption technologies to meet the challenges of water remediation and disinfection. The need and importance of clean water continue to increase as the environmental regulation standards are becoming more and more stringent. The increased range of pollutants in water demand specialized treatment and nanotechnology in this regard can fill the gap where the use of conventional water treatment technologies is either ineffective or not feasible. For the developing countries, there is a distinct opportunity to adopt novel water treatment technologies. Megacities currently lacking extensive water purification infrastructures can adopt on-spot water purification facilities through use of nanotechnologies with relatively low initial costs and avoiding complex water purification operations. Although the emerging nanotechnology for water purification is rapidly replacing the traditional technologies, there are still challenges in their commercialization and practical implementations. The advancement in materials science for the synthesis of cost-effective nanomaterials will decide the progress and fate of nanotechnology application for wastewater treatment. Toxicity issues regarding the use of nanomaterials in the purification processes are to be addressed. These materials during their preparation and application can release and accumulate in the environment and food chain for a longer period of time. Carbon nanotubes, silver, and titania nanoparticles are most suitable for nanotech applications, but they are also toxic for living cells. To be acceptable to regulatory authorities and general public, safe use of these nanomaterials is to be ensured. Nanotech-based water purification is seldom suitable for large-scale operations and in many cases is not competitive with traditional water treatment technologies. In the future, nanotech water treatment promises great potential in centralized and on-spot water purification devices.

References

Ahmed SA, Nasreen N, Sundarrajan S, Abdulrahim Syed SA et al (2013) Advancement in electrospun nanofibrous membranes modification and their application in water treatment. Membranes 3:266–284

Ali Z, Khan A, Ahmad R (2015) The use of functionalized aerogels as a low level chromium scavenger. Microporous Mesoporous Mater 203:8–16

Amit KG, Johal ES, Rath G (2011) Nanotechnology for water treatment. Curr Nanosci 7:640–654

Ba-Abbad MM, Takriff MS, Said M, Benamor A et al (2017) Photocatalytic degradation of pentachlorophenol using ZnO nanoparticles: study of intermediates and toxicity. Int J Environ Res 11(4):461–473

Cloete TE, Kwaadsteniet MD, Botes M, Lopez-Romero JM (2010) Nanotechnology in water treatment applications. Caister Academic Press, Wymondham

Dasgupta N, Ranjan S, Ramalingam C (2017) Applications of nanotechnology in agriculture and water quality management. Environ Chem Lett 15:591–605

Devanathan R (2017) Ion sieving and desalination: energy penalty for excess baggage. Nat Nanotechnol 12(6):500

Humplik T, Lee J, Hern SCO et al (2011) Nanostructured materials for water desalination. Nanotechnology 22:292001

Jesudoss S, Vijaya JJ, Sivachidambaram M, Kennedy L et al (2018) Liquid phase catalytic oxidation of toluene over rich silica and alumina composition of hierarchical ordered ZSM-5 zeolites prepared without organic templates. J Nanosci Nanotechnol 18(8):5367–5379

Liu L, Luo C et al (2017) Reduced graphene oxide (rGO) decorated TiO2 microspheres for visible-light photocatalytic reduction of Cr (VI). J Alloys Compd 690:771–776

Lu CS, Chiu H, Liu CT (2006) Removal of zinc(II) from aqueous solution by purified carbon nanotubes: kinetics and equilibrium studies. Ind Eng Chem Res 45(8):2850–2855

Mondal K (2017) Recent advances in the synthesis of metal oxide nanofibers and their environmental remediation applications. Inventions 2:9

Pendergast MM, Hoek EMV (2011) A review of water treatment membrane nanotechnologies. Energy Environ Sci 4(6):1946–1971

Prathamesh DA (2011) Nanotechnology applications in water purification and wastewater treatment. A review. Nanoscience, engineering and technology, international conference

Ribao P, Rivero MJ, Ortiz I (2017) TiO_2 structures doped with noble metals and/or graphene oxide to improve the photocatalytic degradation of dichloroacetic acid. Environ Sci Pollut Res 24:12628–12637

Safardoust-Hojaghan H, Salavati-Niasari M (2017) Degradation of methylene blue as a pollutant with N-doped graphene quantum dot/titanium dioxide nanocomposite. J Clean Prod 148:31–36

Sajid M, Nazal MK, Ihsanullah, Baig N, Osman AH (2017) Removal of heavy metals and organic pollutants from water using dendritic polymers based adsorbents: a critical review. Sep Purif Technol 191:400–423

Savage N, Diallo MS (2005) Nanomaterials and water purification: opportunities and challenges. J Nanopart Res 7:331–342

Theron J, Walker JA, Cloete TE (2008) Nanotechnology and water treatment applications and emerging opportunities. Crit Rev Microbiol 34:43–69

Wiesner MR, Bottero JY (2007) Environmental nanotechnology: applications and impacts of nanomaterials, 1st edn. McGraw-Hill, New York

Yang K, Xing BS (2010) Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application. Chem Rev 110(10):5989–6008

Yang HY, Han ZJ et al (2013) Carbon nanotube membranes with ultrahigh specific adsorption capacity for water desalination and purification. Nat Commun 4:2220

Chapter 6
Overview of Nanomaterial-Assisted Technologies for Denitrification Processes

Naghmeh Sadat Mirbagheri, Samad Sabbaghi, Pu Chen, and Zahra Bahmani

Contents

6.1 Introduction . . . 166
6.2 Chemical Denitrification Using Nano Zero-Valent Iron . . . 168
  6.2.1 Intrinsic Characteristics of Nano Zero-Valent Iron . . . 169
  6.2.2 The Effect of Operational Conditions on the Nano Zero-Valent Iron Performance . . . 172
  6.2.3 The Effect of Solution Composition on the Nano Zero-Valent Iron Performance 175
  6.2.4 Improving the Selectivity of Nano Zero-Valent Iron Toward Nitrogen Gas . . . 176
6.3 Bimetallic Nanoparticles for Catalytic Denitrification . . . 176
6.4 Photocatalytic Denitrification by Nanomaterials . . . 178
  6.4.1 Addition of Hole Scavengers . . . 180
  6.4.2 Doped Photocatalysts . . . 181
  6.4.3 Composite Photocatalysts . . . 181
  6.4.4 Applying Potential . . . 183
  6.4.5 Other Parameters Affecting the Photocatalytic Denitrification Process . . . 183
6.5 Nanomaterial-Assisted Biological Denitrification Process . . . 184
6.6 Adsorptive Removal of Nitrate by Nanomaterials . . . 185
6.7 Nitrate Removal by Nanomaterial-Assisted Membrane Technologies . . . 186
  6.7.1 Ion Exchange . . . 186
  6.7.2 Electrodialysis . . . 187
  6.7.3 Nanofiltration . . . 188
  6.7.4 Reverse Osmosis . . . 189

N. S. Mirbagheri · Z. Bahmani
Nanochemical Engineering Department, Faculty of Advanced Technologies, Shiraz University, Shiraz, Iran
e-mail: n.s.mirbagheri@shirazu.ac.ir

S. Sabbaghi (✉)
Nanochemical Engineering Department, Faculty of Advanced Technologies, Shiraz University, Shiraz, Iran

Department of Chemical Engineering, University of Waterloo, Waterloo, ON, Canada
e-mail: samad.sabbaghi@uwaterloo.ca; sabbaghi@shirazu.ac.ir

P. Chen
Department of Chemical Engineering, University of Waterloo, Waterloo, ON, Canada
e-mail: p4chen@uwaterloo.ca

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_6

6.8 Nitrate Removal by Nanomaterial-Assisted Capacitive Deionization 190
6.9 Patents Reported on the Removal of Nitrate by Nanomaterial Structures 192
6.10 Summary and Outlook 193
References 195

Abstract Nowadays due to the industrial growth, excessive utilization of agricultural fertilizers, and various ecological changes, the content of nitrate increases in our environmental water. The World Health Organization recommends the permissible nitrate concentration of 10 mg L^{-1} for human consumption. Nitrate concentrations above 10 mg L^{-1} limit can cause major health problems such as blue baby syndrome and formation of carcinogenic nitrosamines in humans. Therefore, the removal of nitrate from contaminated water using various technologies is the topic of many research studies. In this context, denitrification technologies based on organic and inorganic nanomaterials with high efficiency have gained considerable attention. These technologies can be categorized to the degradation and separation processes with varying degrees of efficiency, cost, and ease of operation. An overview of these processes in terms of their performances and issues is reviewed in this chapter. Moreover, the effect of different operational parameters including initial nitrate concentration, nanomaterial loading, nanomaterial durability, solution pH, temperature, and dissolved oxygen on the removal percentage of nitrate is discussed. Finally, advantages and disadvantages of these processes are highlighted to give the readers a complete, comprehensive, and balanced view of the latest technologies for the treatment of nitrate-contaminated waters.

Keywords Nanomaterial · Denitrification process · Water treatment · Nitrate contamination · Nano zero-valent iron · Photocatalytic denitrification · Biological denitrification · Adsorption technology · Membrane technology · Capacitive deionization

6.1 Introduction

Water covers about 70% of the earth but only about 2.8% of this water is fresh. Sources of water on our planet are (I) ground sources such as groundwater, springs, hypothetic zones, and aquifers; (II) precipitation, which includes rain, hail, snow, and fog; (III) surface water such as rivers, streams, and glaciers; (IV) biological sources such as plants; and (V) desalinated seawater. Population growth is a factor that has a direct impact on the amount of water being used around the world and also the quality of this water. As the population increases along with the shift toward an industrial lifestyle, the quality of this water is compromised because of the increase in contaminated water production (Gündüz 2015). Contaminated water can cause many types of diarrheal diseases including cholera and other serious illnesses such as

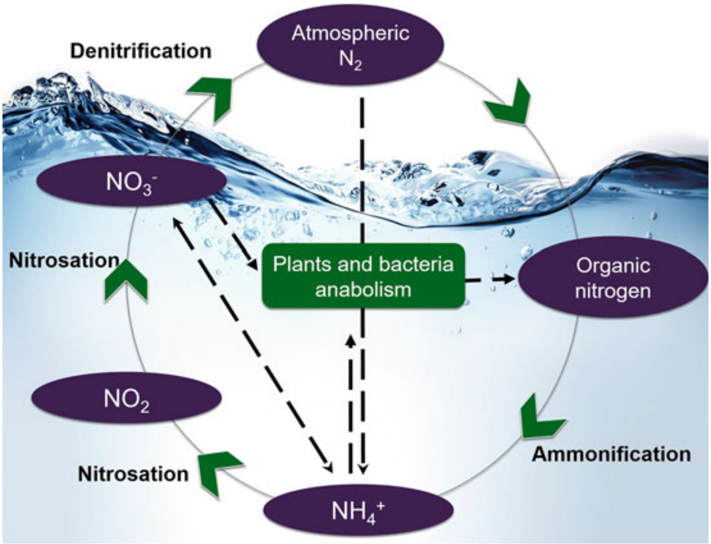


Fig. 6.1 Nitrogen cycle

guinea worm disease, typhoid, and dysentery. Thus, polluted water is not just dirty but also deadly (Bhatnagar and Sillanpää 2011).

Nitrogen is an important element in nature that appears in soil and water in three forms: (I) organic nitrogen, (II) inorganic ammonium (NH_4^+), and (III) nitrogen oxyanions such as nitrite (NO_2^-) and nitrate (NO_3^-). The nitrogen species are naturally exchanged between organisms and the environment as shown in Fig. 6.1. Eutrophication of waters as a result of biological growth and algal blooms in the presence of nitrogen depletes oxygen in water bodies and causes the death of aquatic animals and an irreversible change of the aquatic ecosystem. Moreover, a high concentration of nitrogen oxyanions in our ecosystem has a highly negative impact on human health. Therefore, controlling the nitrogen content in the aquatic environment (nitrogen cycle) is one of the main concerns of the twenty-first-century society (Tugaoen et al. 2017).

Nitrate is an important part of the nitrogen cycle. It is a colorless, odorless, and tasteless substance with high solubility in water (David et al. 2010). Nitrate contamination of water may result from point sources such as sewage disposal systems and livestock facilities as well as nonpoint sources such as fertilized cropland, parks, lawns, and gardens, or naturally occurring sources of nitrogen. Nitrate is highly leachable and readily moves with water through the soil profile. If there is excessive rainfall or over-irrigation, nitrate will leach below the plant's root zone and eventually reach groundwater.

High concentration of nitrate in environmental water can cause overstimulation of growth of aquatic plants and algae. Excessive growth of these organisms can clog water intakes, use up dissolved oxygen, and block light to deeper waters. Therefore, lake and reservoir eutrophication can occur, which produces unsightly scums of algae on the water surface. Algae growth not only consumes all dissolved oxygen which enters the water supply to anaerobic condition but also changes the color and taste of water (Harris et al. 2016). High concentration of nitrate in drinking water is harmful to young infants and leads to "blue baby syndrome." Other illnesses related to the high concentration of nitrate are thyroid, carcinogenic nitrosamine, diabetes, and infectious diseases. The US Environmental Protection Agency has set the maximum contaminant level of nitrate as nitrogen at 10 mg L^{-1} for the safety of drinking water (Hord and Conley 2017). Therefore, removal of excessive quantities of nitrate from drinking water is crucial for water quality and human health.

Removal of excessive nitrate from contaminated water is performed through various technologies. These technologies can be grouped into degrading and separating processes. The degradation-based processes including chemical reduction using Fe^0 as well as catalytic, photocatalytic, and biological denitrification can reduce nitrate to harmless nitrogen gas. However, controlling the operational parameters in these processes is very crucial to prevent the formation of hazardous compounds such as nitride or ammonium. In contrast, the separation-based processes including adsorption, ion exchange, electrodialysis, nanofiltration, reverse osmosis, and capacitive deionization help us to merely separate nitrate from contaminated water and transfer it to a waste stream. Nevertheless, it is not logical and safe to dispose of a large quantity of the separated nitrate along with spent materials into the environment. Therefore, it is necessary to combine the separation-based processes with other technologies in order to completely treat and eliminate the generated secondary wastes from our ecosystem. All these concerns, drawbacks, and possible solutions that have been proposed to effectively and efficiently remove nitrate from contaminated water using pioneer and novel nanomaterial-assisted technologies are discussed in the following sections.

6.2 Chemical Denitrification Using Nano Zero-Valent Iron

In the past two decades, metal nanoparticles with unique properties have attracted significant attention as a favorable reactant for removal of nitrate from water. In this context, nano zero-valent iron (NZVI) has been extensively studied due to its low cost, nontoxicity, and high activity ($E^0 = -0.44$ V) for chemical reduction of nitrate ions. Moreover, the NZVI particles have some advantages compared to ZVI in microscale for removal of nitrate, including (I) an increase in the rate of degradation reaction, (II) a decrease in the required amount of NZVI, (III) the possibility of controlling the release of toxic intermediates, and (IV) a decrease in the production of toxic compounds (Fu et al. 2014).

The NZVI can reduce nitrate contamination of water to nitrite, ammonium, and/or nitrogen gas (6.1, 6.2, and 6.3), while the NZVI might be oxidized to Fe^{2+}, Fe^{3+}, Fe_2O_3, or Fe_3O_4 depending on the reaction conditions. The conversion of Fe^0 to the oxidized forms is the main drawback of this system, and more research is being conducted to find a solution for the regeneration of iron. Among the denitrification reactions, the most desirable one is the complete reduction of nitrate to nitrogen gas (6.3) instead of the generation of nitrite and ammonium by-products (6.1 and 6.2).

$$Fe^0 + NO_3^- + 2\,H_2O \rightarrow NO_2^- + Fe^{2+} + 2\,OH^- \tag{6.1}$$

$$4\,Fe^0 + NO_3^- + 7\,H_2O \rightarrow NH_4^+ + 4\,Fe^{2+} + 10\,OH^- \tag{6.2}$$

$$5\,Fe^0 + 2\,NO_3^- + 6\,H_2O \rightarrow N_2 + 5\,Fe^{2+} + 12\,OH^- \tag{6.3}$$

There are some factors that affect the removal percentage of nitrate from water using NZVI, including intrinsic characteristics of NZVI (e.g., morphology, size, surface area, iron impurities, and oxide film formation), operational conditions (e.g., dissolved oxygen, iron dosage, solution pH, and temperature), and composition of the solution (cationic, anionic, or neutral molecules), which are discussed below (Sun et al. 2016b).

6.2.1 Intrinsic Characteristics of Nano Zero-Valent Iron

Iron intrinsic characteristics such as morphology, size, specific surface area, purity, and corrosion are known to contribute to its performance (Sun et al. 2016b). Therefore, the effect of these factors on the activity and nitrate removal efficiency of NZVI must always be considered.

Morphology and Size

There are two well-known approaches to synthesize NZVI particles: bottom-up and top-down. In the bottom-up method, individual atoms and molecules are gathered to form NZVI particles. In contrast, in the top-down method, granular or microscale iron particles are mechanically or chemically crushed into NZVI particles. These synthesis methods can be generally classified to the chemical and physical method, which lead to variation in average particle size, morphology, activity, and stability of the NZVI (Hwang et al. 2011). Among these methods, borohydride reduction of ferrous salts is a very popular chemical synthesis method because of its low cost, simplicity, feasibility, and production of highly reactive particles (Jamei et al. 2013).

Synthesis of NZVI by the borohydride reduction of ferrous salts consists of four main steps – (I) nucleation, (II) growth, (III) aggregation, and (IV) aging – which are affected by the reductant delivery rate, iron precursor, and reductant concentration

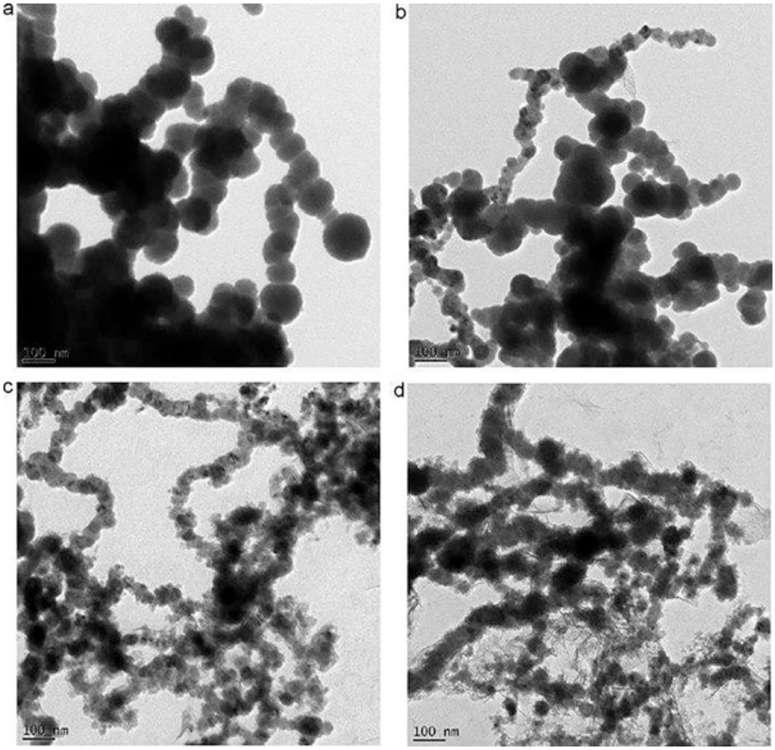


Fig. 6.2 TEM images of the NZVI synthesized under reductant delivery rates of (**a**) 2, (**b**) 5, (**c**) 10, and (**d**) 20 ml min^{-1}. (Reprinted with permission from Hwang et al. 2011)

(Hwang et al. 2011). Therefore, various NZVI particles with different properties and activities can be synthesized by changing these synthesis parameters. For example, different morphologies and sizes were observed in the synthesis of NZVI particles when the delivery rate of the reductant changed from 2 to 20 ml min^{-1}. As can be seen from Fig. 6.2, the morphology of the synthesized NZVI can be spherical (a), non-spherical and scattered (d), or in between (b and c) depending on the delivery rate of reductant (Hwang et al. 2011)

Hwang et al. reported that the nitrate removal efficiency of the NZVI synthesized under the low delivery rate of the reductant was about 35%, while the removal efficiency of the particles improved to about 49% when the delivery rate of the reductant increased to 20 ml min^{-1}. Other experiments revealed that the increase in the concentration of reductant and iron precursor leads to the decrease in the NZVI particle size, and as a result, the removal performance of the NZVI improves. Therefore, to maximize the efficiency of NZVI in the reduction of nitrate, the control of synthesis conditions is very critical (Hwang et al. 2011).

Specific Surface Area

As the chemical reduction reaction occurs at the surface of iron nanoparticles, the surface area of these particles plays an important role in nitrate removal efficiency of NZVI. The surface area can increase by enhancing the amount of iron or by reducing the size of these particles. In general, the chemical denitrification process is expected to improve by enhancing the surface area of NZVI. Hwang et al. reported that the nitrate removal efficiency of NZVI increased from about 35% to 49% when the specific surface area of these particles increased from 8.4 to 45.4 $m^2 g^{-1}$ (Hwang et al. 2011).

Iron Source and Purity

As mentioned before, NZVI can be synthesized through different methods. However, the initial source of iron that is used for the synthesis of these particles can vary in composition and influence the performance of NZVI. For example, synthesis of NZVI through electrolysis method is typically purer than their production by reduction of ore hematite at high temperature, because hematite ore may contain substantial amounts of carbon, silicon, and transition metals that can remain with the produced iron (Sun et al. 2016b). In this context, Liu et al. (2012) studied the nitrate removal efficiency of NZVI prepared by hydrogen reduction of natural goethite and hydrothermal goethite compared with that of the ordinary NZVI. Their results showed that the activity and stability of the NZVI prepared by hydrogen reduction of natural goethite and hydrothermal goethite were higher than the ordinary NZVI because of the existence of Al substitution in goethite. Furthermore, they found that the performances of the NZVI prepared by hydrogen reduction of natural goethite and hydrothermal goethite in the denitrification process were almost pH independent compared with that of the ordinary NZVI. These results demonstrated that the NZVI samples synthesized from different origins have different performances toward the removal of nitrate.

Oxide Layer Coated on Iron Surface

Based on the production time and storage condition, two types of the oxide film may exist on the surface of NZVI. The first kind of film is formed in the production and storage of NZVI in contact with air (Gheju 2011). The other kind of film forms when NZVI is in contact with water or polluted water. Both of these oxide films can play an important role in the performance of NZVI. The pre-existing oxide film is made of an inner film of magnetite, where the electrons can freely move, and an outer film of hematite. In the early stages of reaction when oxide films are formed, the layer of hematite could make the electron and mass transfer difficult and thus reduce the performance of NZVI. Fortunately, partial decomposition (auto-reduction) of this protective film in contact with water can occur that results in electron transfer from NZVI to nitrate ions (Guan et al. 2015).

Formation of the oxide layer on the surface of NZVI in contact with water is well known as iron corrosion. This type of oxide layer can be transferred into a complex mixture of Fe_3O_4, Fe_2O_3, FeOOH, $Fe(OH)_2$, or $Fe(OH)_3$ with time and thus decreases the reactivity of NZVI (Suzuki et al. 2012). In this context, Kim et al. reported that the formation of iron oxides/hydroxides on the surface of NZVI in aqueous solutions results in the desorption of nitrate from the NZVI and a decrease in ammonium generation. Indeed, the presence of hydroxyl groups (FeOOH, $Fe(OH)_2$, or $Fe(OH)_3$) makes the particles' surface charge negative, and thus anion (e.g., nitrate) repulsion occurs (Kim et al. 2013).

6.2.2 The Effect of Operational Conditions on the Nano Zero-Valent Iron Performance

During the chemical reduction of nitrate using NZVI, many interfacial reactions such as dissolution, adsorption, redox reactions, and precipitation may occur on the surface of NZVI either at the same time or sequentially. Operational parameters such as dissolved oxygen, iron dosage, solution pH, pretreatment of iron, and temperature can influence the abovementioned processes and impact the nitrate removal efficiency (Sun et al. 2016b). Therefore, understanding the impact of these parameters is very crucial to provide the best operational condition for the removal of nitrate.

Dissolved Oxygen

The NZVI is mostly used in aqueous systems where dissolved oxygen is present (Shimizu et al. 2012). Dissolved oxygen has a high impact on iron corrosion and thus on the activity of these particles (Sun et al. 2016b). Despite many studies that have been conducted on the impact of dissolved oxygen on NZVI performance, there is no overall conclusion (Tang et al. 2015). Some studies concluded that dissolved oxygen improves the performance of NZVI by increasing iron corrosion (Im et al. 2011; Wang et al. 2010; Yoon et al. 2011), while another study proved the contrary and showed that dissolved oxygen increases the chances of formation of an oxide layer as a surface passivation layer (Yin et al. 2012). As a general concept, it can be concluded that the effect of dissolved oxygen is dependent on the type of removal process (Sun et al. 2016b). In the case of nitrate reduction, a competition between nitrate ions and dissolved oxygen for capturing of electrons must be considered (Zeng et al. 2017). As investigated previously, nitrate reduction by NZVI in the presence of dissolved oxygen is not efficient due to instability and weak performance of Fe^0 in this condition (Zhang et al. 2011). Therefore, the denitrification process using NZVI was suggested to be studied in deoxygenated media. However, Kalil et al. reported that the addition of $CuCl_2$ to nitrate-contaminated water can compensate the negative effect of dissolved oxygen on the performance of NZVI (Khalil et al. 2016).

Iron Dosage

As can be expected, with an increase in iron dosage, the active sites and reactive surface area of NZVI enhance, and thus the performance of these particles improves (Sun et al. 2016b). This positive effect of increasing iron dosage was widely investigated by many research groups (Hwang et al. 2011; Liu et al. 2014d; Hosseini et al. 2011; Bekhradinassab and Sabbaghi 2014). Generally, increasing the dosage of iron enhances the removal of nitrate to an optimum point, but any further increase in iron dosage may not have a positive impact on nitrate removal. For example, it was reported that the nitrate removal percentage of NZVI increased up to 90% when iron to nitrate ratio was about 40:1. Further increase in the concentration of iron did not change the removal percentage of nitrate, and the concentration of nitrate reached the steady state (Liu et al. 2012).

Solution pH

Solution pH has a significant influence on the efficiency of NZVI since the rate of iron corrosion is affected by the solution pH (Bae and Hanna 2015; O'Carroll et al. 2013). As can be seen from Fig. 6.3, Fe^0 is completely stable at pe more than −9 over the entire range of pH 0–14. However, at pe less than −9 and acidic media, it will react with water to form Fe(II), which can be oxidized to Fe(III) in the presence of oxygen. In contrast, at high pH values, Fe(II) can be hydrolyzed to $Fe(OH)_2$, $Fe(OH)_3$, or $Fe(OH)_4^-$, which act as barriers (Sun et al. 2016b). Therefore, at low pH, due to the dissolution of an oxide layer on the surface of iron as well as iron corrosion, a good performance is expected for NZVI (Dong et al. 2010). It should be mentioned that the lowering of pH to very acidic conditions, below pH 4, can cause massive iron dissolution and/or hydrogen bubbling at NZVI interface that reduces the activity of these particles. At high pH, on the other hand, the performance of NZVI reduces due to the mineral precipitation and difficulty in mass transfer. In addition, at high pH, above 8, iron oxide can precipitate on the surface of NZVI and reduce its activity (Bekhradinassab and Sabbaghi 2014). In conclusion, as the best nitrate removal is achieved in acidic media (according to 1–3), the optimum solution pH for the efficient denitrification process by NZVI can be considered in the range of 4–7 (Babaei et al. 2015; Bekhradinassab and Sabbaghi 2014).

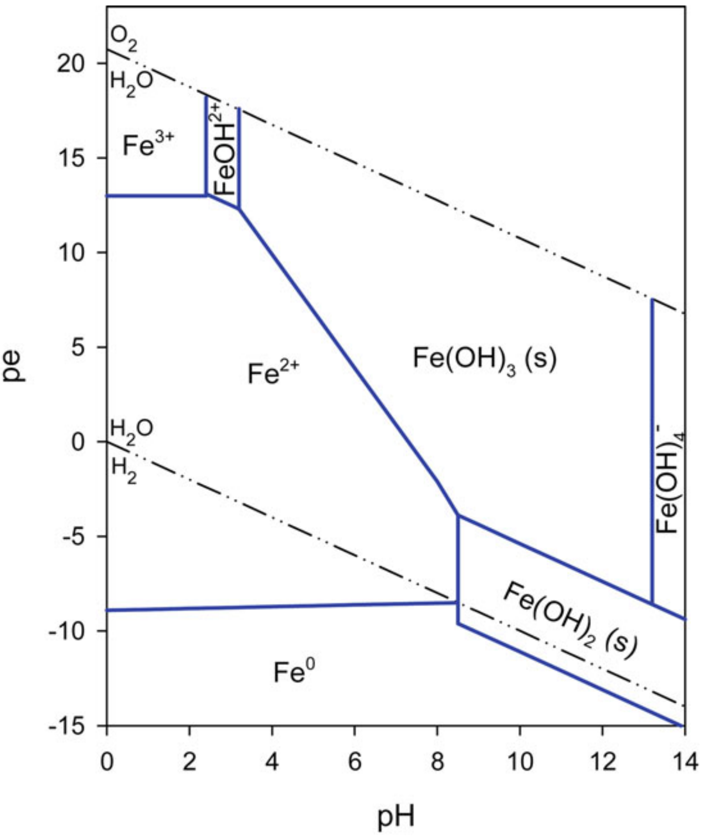


Fig. 6.3 pe-pH diagram for the Fe-H_2O system at 25 °C. The double-dotted dashed line indicates the interference of Fe (aq.) with air (O_2). (Reprinted with permission from Sun et al. 2016b)

Pretreatment of Iron

In order to remove the passivated layer on the surface of NZVI and enhance the performance of these particles, iron pretreatment is necessary before these particles are being used. The common methods employed for activation of NZVI are acid washing, pretreatment with hydrogen gas, and ultrasound pretreatment (Guan et al. 2015; Sun et al. 2016b).

In the acid washing method, acids such as HCl can be used for the removal of the oxide layer. This treatment results in cleaning the surface of the iron, increasing the iron surface area, enhancement of the active sites, and adsorption of H^+ on the surface of the iron. However, in some cases, rapid iron corrosion might lead to precipitation of minerals on the NZVI surface that can reduce the performance of these particles in the long term (Khalil et al. 2017b). Pretreatment with hydrogen gas was also reported to increase the performance of NZVI in the removal of nitrate.

As reported by Liou et al., this treatment increases the concentration of active sites on the iron surface, and thus the removal of nitrate from contaminated water improves (Liou et al. 2005). Ultrasound pretreatment could clean the surface of iron from the precipitates and corrosion products and increase the percentage of active sites by pitting and cracking of the NZVI surface (Geiger et al. 2002). All abovementioned treatments can significantly improve the performance of NZVI in the denitrification process.

Temperature

Temperature enhancement has a positive impact on the denitrification process by NZVI. At high temperatures, the mass transport is accelerated and the adsorption process is more desirable. On the other hand, elevated temperature reduces the activation energy barrier of a redox reaction which indirectly improves the performance of NZVI (Peng et al. 2015).

6.2.3 The Effect of Solution Composition on the Nano Zero-Valent Iron Performance

Besides the NZVI intrinsic properties and operational conditions, the composition of the solution affects the performance of NZVI and removal percentage of nitrate from contaminated water. Therefore, in the following section, the effect of coexisting species will be discussed.

Coexisting of Different Species

A wide range of species might coexist with nitrate in contaminated water. These solutes are anions such as Cl^-, SO_4^{2-}, CO_3^-, and ClO_4^-; cations such as Fe^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, and Mg^{2+}; and natural organic compounds. As previously investigated, these types of contaminants, their exposure time, and concentration can influence the performance of NZVI in the denitrification process. These impacts could be positive either by facilitating the removal of the passive oxide layer or by forming new reactive phases at the surface of NZVI. In contrast, their negative impacts can arise when these species compete with nitrate ions to reduce or accumulate at the surface of NZVI (Sun et al. 2016b). For example, Su et al. studied the removal percentage of nitrate by NZVI from an aqueous solution containing Cd^{2+}. They showed that the presence of Cd^{2+} in the solution results in the formation of Cd islands (Cd^0 and CdO) on the surface of NZVI, which can enhance electron flow from NZVI to nitrate. Therefore, the performance of NZVI in the removal of nitrate and Cd^{2+} is enhanced (Su et al. 2014).

The effect of cationic (Fe^{2+}, Fe^{3+}, and Cu^{2+}) and anionic ions (citrate, oxalate, acetate, ${SO_4}^{2-}$, ${PO_4}^{3-}$, Cl^-, and ${HCO_3}^-$) on the performance of Fe^0 in the reduction of nitrate was also evaluated by Tang et al. (2012). Based on their results, cationic ions lead to the direct or indirect formation of Fe^{2+} ions that have a great potential for nitrate reduction and thus significantly improve the removal of nitrate. The anionic ions also enhanced nitrate reduction in the order of citrate > acetate > ${SO_4}^{2-}$ > Cl^- ≈ ${HCO_3}^-$ ≈ oxalate≫ ${PO_4}^{3-}$. Therefore, the chemical denitrification in a real sample such as contaminated water containing these ions is not problematic.

6.2.4 *Improving the Selectivity of Nano Zero-Valent Iron Toward Nitrogen Gas*

As mentioned before, chemical reduction of nitrate by NZVI leads to the formation of nitrite, ammonium, and/or nitrogen gas. The produced ammonium as a hazardous compound that easily dissolves in water can cause irritation and burns in humans. Therefore, many efforts are being conducted to improve the properties and reactivity of NZVI in the denitrification process toward the production of nitrogen gas. Some of these efforts were devoted to make a composite of NZVI with various compounds, for example, composite of NZVI with metals (e.g., Cu, Pd, Pt, Ag, and Ni) as a monometallic or bimetallic/NZVI composite (Li et al. 2017; Hosseini et al. 2011; Hamid et al. 2015), semiconductors (will be discussed in the next section), as well as immobilization of NZVI onto clay (Zhang et al. 2011), zeolite (Zeng et al. 2017), carbon-based materials (Babaei et al. 2015; Khalil et al. 2017a), resin (Shi et al. 2013), and silica (Bekhradinassab and Sabbaghi 2014). In another approach, the use of biomolecules in combination with NZVI was reported to treat the generated ammonium and convert it into nitrogen gas (Peng et al. 2015). These approaches are discussed in the following sections.

6.3 Bimetallic Nanoparticles for Catalytic Denitrification

Catalytic denitrification over a solid catalyst is considered as an extension of the chemical denitrification process. Although several catalyst types including monometallic and bimetallic catalysts have been extensively investigated, the most common catalytic system for the denitrification process is bimetallic catalysts. The bimetallic catalysts consist of a precious metal (Pt or Pd) and a promoter (Cu, Ni, Fe, Sn, In, Ag), which may be a transition metal or a metal oxide (Barrabés and Sá 2011). The function of the promoter is to reduce nitrate to nitrite by a redox process to start the catalytic process, while the noble metal plays an important role in maintaining the transition metal in the metallic state and reducing nitrite by activated

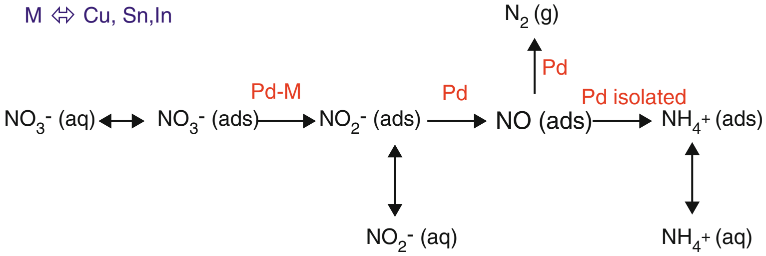


Fig. 6.4 Mechanism of the catalytic denitrification using bimetallic catalysts. M is a metal and acts as a promoter. (Reprinted with permission from Barrabés and Sá 2011)

hydrogen (Sun et al. 2012). Among all the bimetallic catalysts, supported palladium catalysts with copper or tin as a promoter exhibited the highest activity for the catalytic denitrification (Matatov-Meytal and Sheintuch 2005). However, the use of palladium for the catalytic denitrification process has a major environmental impact (Chiueh et al. 2011).

The mechanism of bimetallic catalytic denitrification is first described by Tacke and Vorlop, and it has remained unchanged since then (Tacke and Vorlop 1993). Based on this mechanism (Fig. 6.4), nitrate is reduced to nitrogen in several steps involving the formation of nitrite, nitric oxide (NO), and nitrous oxide (N_2O) as intermediate products. The first reaction step, the reduction of nitrate to nitrite, occurs on palladium only in the presence of a promoter, whereas no such promoter is necessary for the subsequent reduction of nitrite to nitrogen and ammonium (Barrabés and Sá 2011). In this process, hydrogen gas is added into the reaction medium by a gas flowmeter not only as a reductant but also to maintain the activity of the catalyst (Hamid et al. 2015)

The main concern in catalytic denitrification is the control of activity and selectivity of the catalyst to prevent both incomplete hydrogenation to nitrite and hydrogenation to ammonium. To enhance the catalytic activity and selectivity of the bimetallic systems, extensive studies have been focused on the determination of proper support materials, which significantly affect the catalytic properties. γ-Al_2O_3 is the most used support due to its unique surface properties, phase composition, and local microstructures. Other supports including organic or inorganic membrane, active-based materials, zeolites, resins, and polymers have also been used for this purpose (Sun et al. 2010)

The efficiency of the catalytic denitrification process is also affected by the hydrogen flow rate, solution pH, catalyst loading, dissolved oxygen, medium temperature, and catalyst longevity, which vary based on the type of catalytic system. As reported by Liu et al., the increase of the Fe^0/Pd/Cu dosage enhanced the rate of nitrate removal as a result of more contact chance between nitrate ions and the composite (Liu et al. 2014a). Moreover, the use of optimum dosage of the composite effectively removed nitrate and reduced the ammonium formation. The nitrate removal efficiency evaluated at pH range from 3.5 to 9 revealed that the increase in pH value resulted in a decrease in nitrate removal rate, as discussed in section

"Solution pH". They also showed that the removal rate of nitrate improved with the increase of the reaction temperature and at the lower content of dissolved oxygen, as discussed in section "Dissolved oxygen". In another work, Jung et al. reported that the selectivity of the maghemite/Cu/Pd catalyst toward nitrogen gas was slightly higher at lower hydrogen flow because the high content of hydrogen molecules at the surface of Pd sites promotes the formation of ammonium (Jung et al. 2012). Hamid et al. also investigated the effect of different operational parameters on the performance of the Cu-Pd/NZVI catalyst. The obtained results demonstrated that with the increase of the Cu and Pd loading, respectively, to 1.5% and 0.5%, the nitrogen selectivity increased. They also reported that the catalytic activity of the Cu-Pd/NZVI is strongly influenced by leaching and aggregation of bimetals as well as the oxidation of NZVI (Hamid et al. 2015).

6.4 Photocatalytic Denitrification by Nanomaterials

The photocatalytic reduction is a transformative technology which can be used at the nanoscale for reducing nitrate to harmless nitrogen gas. The photocatalytic behavior of materials was stated for the first time by Fujishima and Honda in 1972 (Fujishima and Honda 1972). After that report, many researchers devoted their time to study photooxidation processes by different photocatalysts (Tugaoen et al. 2017). Photocatalysts have the ability to enable redox reactions by creating photogenerated electrons and holes (Doudrick et al. 2013). In the photocatalytic process, the photocatalyst adsorbs photons with energy equal to or higher than its band gap energy (Tugaoen et al. 2017). Consequently, the electrons from the valence band of a semiconductor are excited to the empty conduction band (e_{cb}^-). After this electron excitation, a vacancy with positive charges (h_{vb}^+) is generated (Fig. 6.5a). The

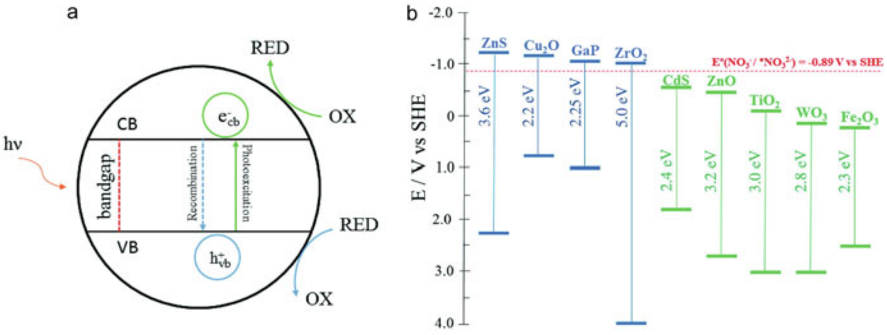


Fig. 6.5 (**a**) Schematic of charge carrier (e_{cb}^-/h_{vb}^+) separation and a redox reaction as a result of photocatalytic excitation. (**b**) Connection between band structure of semiconductors, their redox potentials, and nitrate reduction potential vs standard hydrogen electrode. (Reprinted with permission from Tugaoen et al. 2017)

photogenerated charge carriers must then transfer from the bulk to the surface of the photocatalyst, where they involve in redox reactions (Cai and Feng 2016). However, the lifetime of these charges is very short, and they can be quickly and easily recombined (6.4). This recombination is the main drawback of photocatalysis and has a negative impact on the efficiency of the photocatalyst in the denitrification process.

$$e^-_{\mathrm{cb}} + h^+_{\mathrm{vb}} \rightarrow \text{semiconductor} + \text{heat} \tag{6.4}$$

Besides the lifetime of the photogenerated charges, the energy of valence and conduction band of the photocatalyst must be adequately matched with the required energy for the denitrification process. This means that the conduction band is required to have a more negative potential than the reducing species (e.g., nitrate) and the valence band is required to have a more positive potential than the oxidizing species (Fig. 6.5b) (Tugaoen et al. 2017).

The overall photocatalytic denitrification reactions of nitrate to nitrite, ammonium, and nitrogen at the surface of a photocatalyst are presented below (6.5, 6.6, and 6.7). However, to understand the mechanistic steps involved in this photocatalytic process and to enhance selectivity toward nitrogen production, more considerations are required (Tugaoen et al. 2017).

$$\mathrm{NO_3^-} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-_{cb}} \rightarrow \mathrm{NO_2^-} + \mathrm{H_2O} \tag{6.5}$$

$$\mathrm{NO_3^-} + 10\,\mathrm{H^+} + 8\,\mathrm{e^-_{cb}} \rightarrow \mathrm{NH_4^+} + 3\,\mathrm{H_2O} \tag{6.6}$$

$$2\,\mathrm{NO_3^-} + 12\,\mathrm{H^+} + 10\,\mathrm{e^-_{cb}} \rightarrow \mathrm{N_2} + 6\,\mathrm{H_2O} \tag{6.7}$$

Since the majority of reported works have used $\mathrm{TiO_2}$ for the photocatalytic denitrification process, the main focus of the following discussion will be the $\mathrm{TiO_2}$-based photocatalysts in nanometer scale (Tugaoen et al. 2017).

In the earlier studies of the denitrification process using a pure $\mathrm{TiO_2}$ photocatalyst, no conversion of nitrate was reported (Ranjit and Viswanathan 1997). The inactivity of the pure $\mathrm{TiO_2}$ was related to the fast recombination of photogenerated electrons and holes in this photocatalyst as a result of its wide band gap (Tugaoen et al. 2017). Under this condition, the photogenerated charges rarely participate in the reduction of nitrate, and thus the efficiency of the process reduces. Various strategies have been developed to overcome the drawback and also to improve the selectivity of the $\mathrm{TiO_2}$ photocatalyst toward nitrogen production, which are presented in the following sections.

6.4.1 Addition of Hole Scavengers

As mentioned before, it is essential to minimize the recombination of the photogenerated charges in order to improve the photocatalytic performance of pure TiO_2 in the reduction of nitrate ions (Tugaoen et al. 2017). A possible solution to overcome this problem is the addition of a hole scavenger or sacrificial electron donor to the reaction medium. The most common hole scavengers are organic compounds such as methanol, oxalic acid, and formic acid (Tugaoen et al. 2017). Among them, formic acid has the most desirable performance because of its favorable interaction with the holes and generation of $CO_2^{\bullet -}$ (6.8), which acts as a reducing mediator (Fig. 6.6a). In addition, formic acid with $pK_a = 3.75$ can release H^+, which is one of the key factors for selective reduction of nitrate to nitrogen gas (Luiz et al. 2012; Kobwittaya and Sirivithayapakorn 2014; Lozovskii et al. 2009; Ren et al. 2015; Sun et al. 2016a).

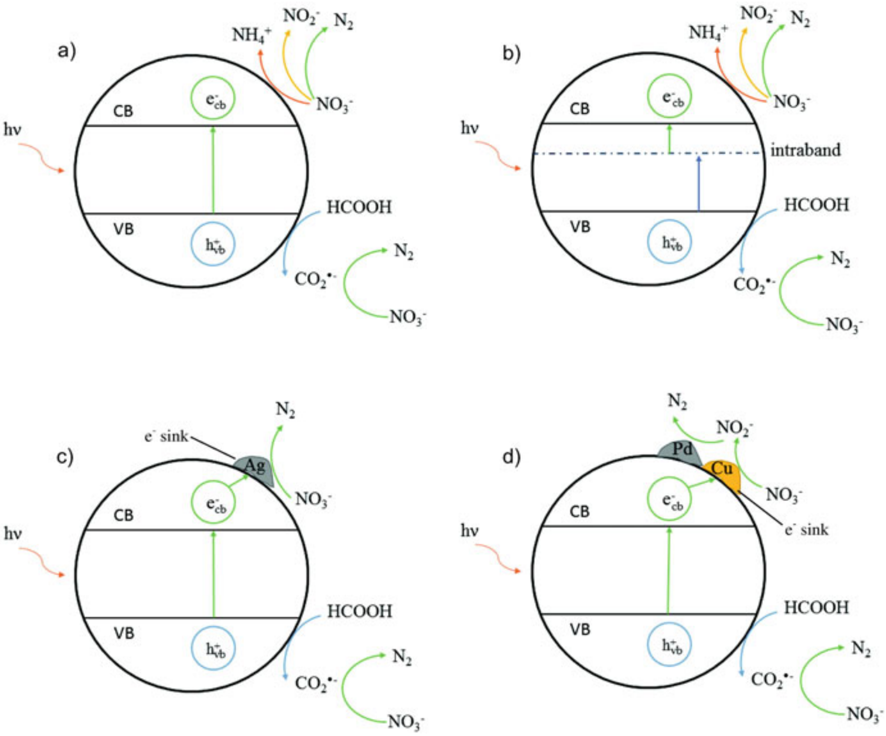


Fig. 6.6 Chemical denitrification process on the (**a**) pure TiO_2, (**b**) doped TiO_2, (**c**) metallic/TiO_2 composite, and (**d**) bimetallic/TiO_2 composite. (Reprinted with permission from Tugaoen et al. 2017)

$$\mathrm{HCOO^-} + h_{\mathrm{vb}}^{+} \rightarrow \mathrm{H^+} + \mathrm{CO_2^{\cdot -}} \tag{6.8}$$

Therefore, the overall photocatalytic reduction of nitrate in the presence of formic acid can be expressed as follows:

$$4\,\mathrm{NO_3^-} + 2\,\mathrm{HCOOH} + 2\,\mathrm{H^+} \rightarrow \mathrm{NH_4^+} + 4\,\mathrm{CO_2} + 3\,\mathrm{HO_2} \tag{6.9}$$

$$\mathrm{NO_3^-} + \mathrm{HCOOH} \rightarrow \mathrm{NO_2^-} + \mathrm{CO_2} + \mathrm{HO_2} \tag{6.10}$$

$$2\,\mathrm{NO_3^-} + 5\,\mathrm{HCOOH} + 2\,\mathrm{H^+} \rightarrow \mathrm{N_2} + 5\,\mathrm{CO_2} + 6\,\mathrm{HO_2} \tag{6.11}$$

Based on the reaction mentioned above (6.9, 6.10, and 6.11), the theoretically stoichiometric ratio of formic acid to nitrate as 2.5 is essential for complete nitrate reduction to nitrogen gas. However, in practice, this value depends on the type of photocatalyst and its available sites. For example, complete conversion of nitrate to ammonium and nitrogen gas was achieved in a solution containing 100 ppm of nitrate and 0.04 M formic acid using 0.5 g L^{-1} of the carbon-modified TiO_2 nanoparticles (Lozovskii et al. 2009).

6.4.2 Doped Photocatalysts

Aside from the addition of hole scavengers, modification of the semiconductor band gap through its doping with different elements has also been reported as another strategy to improve the photocatalytic properties of a pure semiconductor in the denitrification process. In the case of TiO_2, metal dopants are mostly replaced with titanium atoms via substitutional doping, while nonmetal dopants can either replace oxygen atoms or be inserted into the TiO_2 lattice via interstitial doping (Akple et al. 2015). As a result of this modification, higher selectivity toward nitrogen (Girish Kumar and Koteswara Rao 2015) and improved conversion efficiency compared to the pure TiO_2 were obtained (Dozzi and Selli 2013). Figure 6.6b shows that doping TiO_2 leads to the generation of an intraband level within the doped TiO_2 that requires less irradiation energy (Ansari et al. 2016). Therefore, this strategy also makes the process more economical and environmentally friendly (Dozzi and Selli 2013; Shinde et al. 2011).

6.4.3 Composite Photocatalysts

Another strategy to improve the efficacy of the pure TiO_2 in the photocatalytic denitrification process is to make a composite of the photocatalyst with other materials. This composite can be made by combining a metal or two metals (mostly noble metals) with the photocatalysts, which are known as monometallic and bimetallic composite, respectively. Based on the synergistic effects, when multiple materials produce a composite, the combined materials altogether show different or rather better properties than each of the individual materials (Tugaoen et al. 2017). Due to the lower work function of noble metals, and higher electron affinity, than the TiO_2 photocatalyst, the noble metals act as an electron sink. Therefore, the photogenerated electrons within the photocatalyst are transferred to the metal surface where they are used as a reducing agent for the denitrification process. Indeed, this strategy significantly extends the lifetime of e_{cb}^{-} and reduces the recombination rate of the photogenerated charges within the TiO_2 semiconductor (Fig. 6.6c, d) (Tung 2014; Kochuveedu et al. 2013).

Monometallic composites are the most prevalent types of denitrification photocatalysts and show different behaviors and performances based on their metal type. The most common metals that have been used for this purpose are fourth-period transition metals (e.g., iron, cobalt, nickel, copper), platinoids (e.g., platinum, palladium, ruthenium), and noble metals (e.g., gold and silver) (Tugaoen et al. 2017). Among them, a composite made of NZVI and TiO_2 has been widely studied. As mentioned in Sect. 6.2.4, the NZVI/TiO_2 composite showed a higher selectivity toward nitrogen gas than NZVI and pure TiO_2. Although the mechanism of denitrification by the NZVI/TiO_2 composite follows the conventional chemical reduction pathways, the interface with TiO_2 synergistically affects the process in two ways. First, higher amounts of adsorbed N-intermediates on the surface of TiO_2 than the coverage of reductant species leads to the evolution of nitrogen gases. Second, the photogenerated electrons in the TiO_2 are not only involved in the denitrification process but also contribute in the recovery of the oxidized iron species to NZVI (Liu et al. 2014c; Pan et al. 2012). Copper is another fourth-period metal that has been used in TiO_2 composites. Copper facilitates nitrate reduction through making a complex with nitrogen species and acting as a reducing center for nitrate. However, the complete reduction of nitrate to ammonium or nitrogen gas is only achieved in acidic conditions (Sá et al. 2009; Wehbe et al. 2009).

The use of platinoids in TiO_2 composite can influence the reductive mechanism and change the photocatalyst performance (Shin et al. 2014). These different performances observed for the platinoids/TiO_2 composites are related to the size and morphology of the metallic component of the composite, as well as the intrinsic capability of that metal to stabilize the H_{ads} for participation in the denitrification process rather than other reactions such as the hydrogen evolution reaction (Tugaoen et al. 2017). In the case of noble metals, gold and silver have been used to produce monometallic TiO_2 composites for the denitrification process in the presence of hole scavengers. Among them, the Ag/TiO_2 composites showed a better nitrate conversion than Au/TiO_2 composites (Wu et al. 2009). However, the reported data are not sufficient to better understand the role of noble metals in combination with TiO_2 in the photocatalytic denitrification process (Tugaoen et al. 2017).

When two of the metals mentioned above are used together to create a composite, a bimetallic composite is obtained, which is the most promising approach for the denitrification of drinking water (Tugaoen et al. 2017). As mentioned before, the use of copper in TiO_2 composites can hardly lead to the formation of ammonium or nitrogen gas. On the other hand, low conversion efficiency is typically observed for the reduction of nitrate to nitrite by platinoid/TiO_2 composites. Therefore, combining copper and platinoids with TiO_2 was reported to enhance the overall performance of TiO_2 in the photocatalytic denitrification process (Sá et al. 2012).

6.4.4 Applying Potential

Another possible way to reduce the recombination of photogenerated charges and to enhance the photocatalytic activity of photocatalyst in the denitrification process is to use an electrochemical method. In this method, a photocatalyst is used as a photoelectrode and a constant current or defined potential is applied through the photocatalyst to separate the charge carriers by an external electrical circuit (Garcia Segura and Brillas 2017). The effect of nitrate photocatalytic reduction with the help of a photocathode has been studied in a few research works. The two important benefits of this method are a great performance of photocatalyst without using hole scavengers and also good selectivity in a quasi-neutral pH environment (Paschoal et al. 2013; Wang and Turner 2013; Liu et al. 2014b).

6.4.5 Other Parameters Affecting the Photocatalytic Denitrification Process

It is clear that the irradiation source is one of the fundamental components of all photocatalytic processes. Contrary to what it looks like, selection of an appropriate light source has a significant influence on the generation of charge carriers. Hg and Xe lamps and natural sunlight irradiation are the most popular irradiation sources that have been used for photocatalytic denitrification process. It is worth to consider that the direct photolysis of nitrate may also happen under light irradiation (Tugaoen et al. 2017). The pH of the solution is another important factor affecting the photocatalytic process. The solution pH can change the photocatalyst surface charge and thus its adsorption properties toward nitrate ions. In addition, several steps of the denitrification process are affected by the solution pH, especially H^+ concentration. Based on the investigation, the solution pH of about 3 is an optimal condition for this purpose (Tugaoen et al. 2017). Finally, the presence of different ions in contaminated water and their influence on the overall efficiency of the process as well as the possibility of fouling or dissolving of photocatalysts during a prolonged operation should also be taken into consideration (Tugaoen et al. 2017).

6.5 Nanomaterial-Assisted Biological Denitrification Process

The biological denitrification process, which is driven either by heterotrophic or autotrophic microorganisms, is one of the most promising technologies for the reduction of nitrate to innocuous nitrogen gas. The main concerns in the biological denitrification are the slow initial start-up as well as the slow transfer of the treated water to potable water due to the potential contamination of the treated water with the microorganisms and their by-products (Fig. 6.7).

The biological denitrification process by heterotrophic microorganisms is performed in the presence of organic substrate as an electron donor to rapidly grow and reduce the nitrate as an electron acceptor. Therefore, the heterotrophic biological denitrification is suitable in the water by sufficient organic carbon source. The most prominent organic substrates for this purpose are glucose, methanol, ethanol, and acetic acid. For example, the reduction of nitrate using a heterotrophic microorganism in the presence of ethanol is shown in (6.12) (Beiki et al. 2016).

$$5\,C_2H_5OH + 12\,NO_3^- \rightarrow 6\,N_2 + 10\,CO_2 + 9\,H_2O + 12\,OH^- \tag{6.12}$$

In contrast, autotrophic microorganisms convert nitrate to nitrogen using inorganic carbon sources such as CO_2 and HCO_3^- for bacterial growth and inorganic electron donors such as sulfur or hydrogen. The autotrophic reduction of nitrate in the presence of hydrogen is shown in (6.13).

$$5\,H_2 + 2\,NO_3^- \rightarrow N_2 + 4\,H_2O + 2\,OH^- \tag{6.13}$$

In comparison with heterotrophic denitrification, removal of nitrate using autotrophic microorganisms not only is cost-effective but also produces less sludge and reduces the need of posttreatment processes (Beiki et al. 2016).

As mentioned in Sect. 6.2.4, the NZVI particles have been used in combination with microorganisms for reduction of nitrate (Peng et al. 2015; Beiki et al. 2016). In the microbial denitrification process, NZVI particles can directly donate their electrons to nitrate (1–3) or indirectly by the generation of hydrogen that acts as an

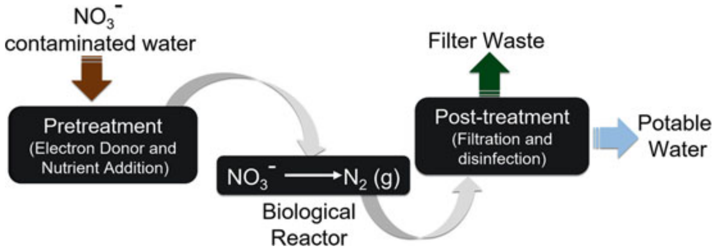


Fig. 6.7 Schematic illustration of the biological denitrification process

electron donor source and reduces the nitrate ions (6.13). Other nanomaterials such as magnetic iron oxide (Ni et al. 2013), bimetallic nanoparticles (An et al. 2010), and nanocrystalline PbO_2 (Mook et al. 2013) have also been used in the biological denitrification process.

Operational parameters such as the initial nitrate concentration, solution pH, dissolved oxygen, and temperature play important roles in the microbial reduction of nitrogen. As can be expected, the initial concentration of nitrate must be comparable with the microorganism's activity, which means that the excessive increase of nitrate concentration can reduce the performance of bacteria in the denitrification process. In the case of solution pH, it was demonstrated that in alkaline media, pH above 8, accumulation of nitrate occurs in the reactor and denitrification is not accomplished due to the inhibitory effect of hydroxyl anions on the activity of microorganisms (Zhu and Getting 2012; Jiang et al. 2013; Liu et al. 2014d). The high dissolved oxygen has a negative impact on the performance of the microorganisms in the removal of nitrate. Therefore, biological denitrification is mostly performed at a low concentration of oxygen (2 mg L^{-1}) (Beiki et al. 2016). The operational temperature has a significant impact on the growth and metabolic activity of microorganisms in the denitrification process. The biological removal of nitrogen was not effective at temperatures below 7 °C, and this process promotes with the increase of the temperature to 35 °C. However, further increase of the temperature to 40 °C reduces the biological denitrification (Chen et al. 2016; Beiki et al. 2016).

6.6 Adsorptive Removal of Nitrate by Nanomaterials

In the adsorption method, a material is used as an adsorbent to remove contaminants such as nitrate from water by adsorbing these pollutants onto its surface. In comparison with the other methods of nitrate removal, adsorption has significant advantages of low-energy consumption, flexibility in operation, as well as a short treatment cycle. It should be noted that the selection of appropriate adsorbents for efficient removal of nitrate from different media is very important. There are various adsorbents that have been proved effective for this aim such as carbon-based sorbents, natural sorbents, synthetic adsorbents, bio-sorbents, miscellaneous adsorbents, agricultural wastes, and industrial wastes. Some of these adsorbents in nanometer size are presented below.

Synthesis of zero-valent aluminum in nanometer scale has been reported as an efficient adsorbent for removal of nitrate. Bhatnagar et al. reported the high potential of nano zero-valent aluminum in the adsorptive removal of nitrate at pH 4.4. The thermodynamic investigation suggested that the interaction of nitrate and nano-alumina is endothermic in nature (Bhatnagar et al. 2010). In another work, Azadbakht et al. extracted nanocrystalline cellulose by acidic hydrolysis of sugarcane bagasse that was considered as a proper nitrate nano-adsorbent due to its nontoxicity, low density, high surface area, and modifiable surface properties. Among different experimental factors such as solution pH, the initial concentration of species, and contact time, the initial concentration of nitrate has the highest influence on the removal efficiency of the nanocrystalline cellulose. As it was expected, the nitrate removal percentage of the nanocrystalline cellulose was high when the surface charge of this compound was positive (Azadbakht et al. 2016).

6.7 Nitrate Removal by Nanomaterial-Assisted Membrane Technologies

Membrane technology for separation of nitrate from contaminated water consists of ion exchange, electrodialysis, nanofiltration, and reverse osmosis processes (Pintar et al. 2001). The main concern in these processes is a selection of suitable membrane with high selectivity toward nitrate and excellent durability against fouling. The composition of contaminated water is also a key factor in these processes and determines the necessity of pretreatment and posttreatment processes, membrane regeneration efficiency, chemical usage, and waste disposal.

6.7.1 Ion Exchange

The most commonly used technology for removal of nitrate from drinking water is ion exchange. Ion exchange process for denitrification involves passage of nitrate-contaminated water through a strong base anion exchange resin on which nitrate ions were exchanged with other ions at the surface sites of the resin until it is exhausted (Fig. 6.8). This process is favorable for communities that do not have the high technology and expensive machinery to manage the removal of nitrate from contaminated water.

In order to improve the efficiency of the denitrification process by the ion exchange technology, a novel class of hybrid media consisted of aluminum (hydr) oxide nanoparticles inside the pores of a strong base ion exchange resin was recently proposed, which is based on the exchange of nitrate with chloride ions (Markovski et al. 2017). In another work, an ion exchange nanopaper was produced from nano-

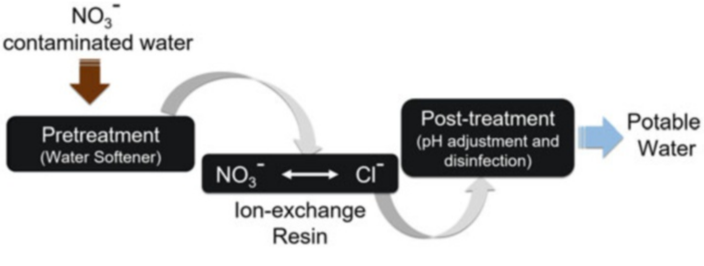


Fig. 6.8 Schematic illustration of ion exchange process for removal of nitrate

fibrillated cellulose to take the advantages of adsorption and membrane processes for effective removal of nitrate (Mautner et al. 2016). To minimize the problems associated with membrane fouling in this system, the nano-fibrillated cellulose was modified with quaternary ammonium groups to obtain. The obtained results with respect to the membrane permeate and nitrate adsorption demonstrated that the modified membrane could successfully capture the nitrate ions from contaminated water during dynamic filtration experiments (Mautner et al. 2016).

6.7.2 *Electrodialysis*

In electrodialysis method, separation of nitrate occurred with the help of semipermeable ion-selective membranes and under the influence of an electric potential. Application of an electric potential between the two electrodes causes an electric current to pass through the solution, which in turn results in a migration of cations and anions (e.g., nitrate) toward the negative and positive electrodes, respectively. The membranes used in electrodialysis are anion and cation exchange membranes that are placed alternately between the negative and positive electrodes (Fig. 6.9).

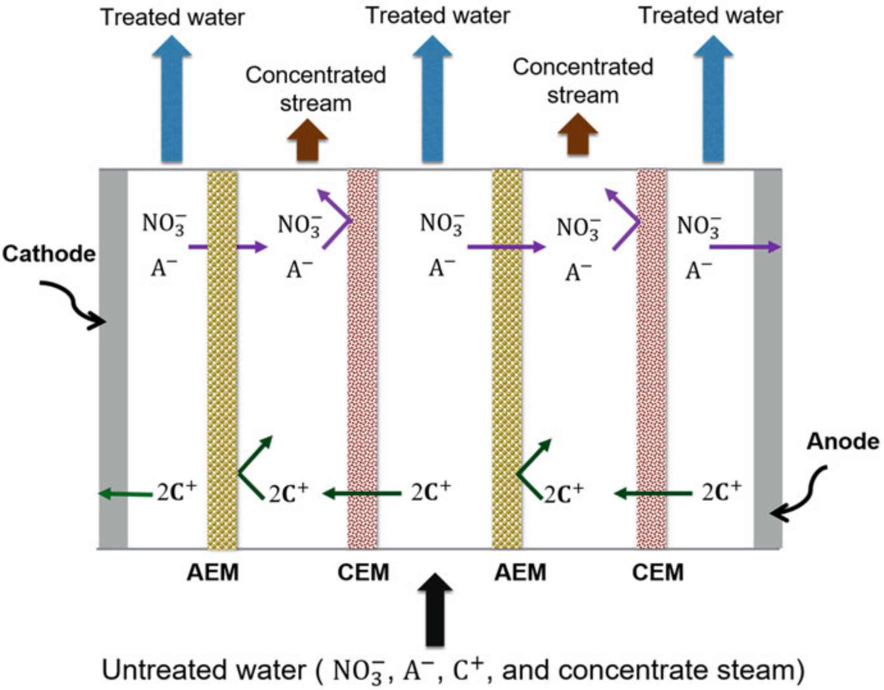


Fig. 6.9 Schematic illustration of electrodialysis for removal of nitrate. AEM, CEM, A^-, and C^+ are anion exchange membrane, cation exchange membrane, anion, and cation, respectively

In the electrodialysis of contaminated water, multivalent ions such as SO_4^{2-} can simultaneously be removed with nitrate. However, too much removal of SO_4^{2-} from the feed water leads to the precipitation of $CaSO_4$ in the concentrated compartment and reduces the performance of the electrodialysis process. Therefore, to avoid precipitation in the concentrated stream and to achieve the drinking water standards, a high selective anion membrane is required in the denitrification process. For this purpose, the surface of the anion exchange membrane was modified with a nano-film of polydopamine. This modification provided a negatively charged layer on the surface of the anion exchange membrane that improved the selectivity toward nitrate ions (Vaselbehagh et al. 2015).

Aside from the membrane selectivity, the operational conditions such as solution pH, flow rate, ion concentration, and applied electric potential have a significant impact on the efficiency of the denitrification process by electrodialysis. As reported previously, the most effective pH for removal of nitrate by electrodialysis method was between 3 and 5, because the adsorption and distribution of nitrate ions among the charged sites on the membrane surfaces are affected by pH. On the other hand, the adsorption of ions on the membrane surface is under the influence of applied potential. At high potential, the adsorbed ions are released, and regeneration of the membranes may occur, while at low potential, the exchange of ions is performed (Wisniewski et al. 2002). Therefore, the solution pH and applied potential must be optimized to effectively remove nitrate ions.

Fouling is minimal in electrodialysis because the feed water does not pass through the membranes, which means that the membranes do not serve as a filter in this process. However, any fouling can be removed using electrodialysis reversal process. In this approach, freshwater is sent to the compartments previously filled with concentrated waste streams, and then the polarity of the system is reversed. The change in the polarity forces the adsorbed ions to move in the opposite direction through the membranes and thus reduces membrane fouling.

6.7.3 Nanofiltration

Nanofiltration is a pressure-driven technology that is mostly used for groundwater treatment and purifying drinking water by reducing water hardness using a semipermeable membrane with the ability to reject particles as small as one nanometer. The rejection of ions by nanofiltration membranes is the consequence of interactions between solution species and the membranes under operational conditions. As it is known, choosing a right membrane is an important step in the nitrate removal by nanofiltration. For this purpose, a membrane with tight pores (less than 2 nm), negative charge, and high permeability toward nitrate ions is more favorable (Sancho et al. 2016).

Two types of negatively charged nanofiltration membranes that have been used in the denitrification process are NF90 and NF270 manufactured by Dow-FilmTec. The NF90 is a dense membrane with a tight porous structure that has a high rejection even to monovalent ions, while the NF270 is a loose membrane. According to the manufacturer's information, the NF90 membrane is designed to remove a high percentage of nitrate ions. In contrast, the use of NF270 with low ion rejection capability is suitable when the nitrate concentration in water barely exceeds the standard limit because of its lower ion rejection. However, higher amounts of flux, stability, and permeability, as well as less fouling, were obtained by NF270 than the NF90 (Hoinkis et al. 2011).

The influence of different factors and operational parameters on the nitrate removal efficiency of the nanofiltration membranes was thoroughly studied (Dizge 2014). The results showed that with the increase of flow rate at a high concentration of nitrate, the efficiency of the membrane decreases. It was also proven that the high concentration of a salt (e.g., NaCl) reduces the rejection of nitrate ions, whereas the membrane permeance to ions increases (Reig et al. 2016). Another study revealed that the impact of pH on nitrate retention was mostly independent, and the retention was highly dependent on the membrane type (Richards et al. 2010).

Since the membrane surface characteristics are the key factors in the membrane exclusion, Ghaee et al. fabricated a thin-film nanocomposite polyamide membrane. The membrane was then modified with zeolite nanoparticles to enhance the performance of the nanofiltration in the denitrification process. The zeolite/thin-film nanocomposite membrane showed high nitrate rejection while maintaining high water flux due to the improvement in the surface hydrophilicity and induction of negative charges on the membrane surface (Ghaee et al. 2017).

To reduce the membrane fouling in the nanofiltration process, modification of the surface of NF270 membrane has been recommended. This modification increases the resistance of the membrane against fouling and also improves membrane functionality and selectivity. Moreover, it can alter the hydrophilicity, roughness, permeability, and surface charge of the membrane (Juholin et al. 2018). In this context, Juholin et al. have recently reported that the modification of NF270 with ZnO nanoparticles reduced the reversible fouling of the membrane, though it did not significantly change the relative flux, permeability, and removal efficiency of the system. In addition, some other challenges such as the high tendency of ZnO to wear off from the membrane surface and its short lifetime were observed in this system (Juholin et al. 2018).

6.7.4 Reverse Osmosis

Reverse osmosis can be used for simultaneous removal of multiple contaminants of water such as anions, particles, and organic constituents. In this process, water is moved across the membrane against the concentration gradient, from lower concentration to higher concentration. For this purpose, a pressure is exerted on the side with the concentrated solution to force the water molecules across the membrane to the freshwater side without making any changes in the molecular structure of compounds (Fig. 6.10) (Malaeb and Ayoub 2011).

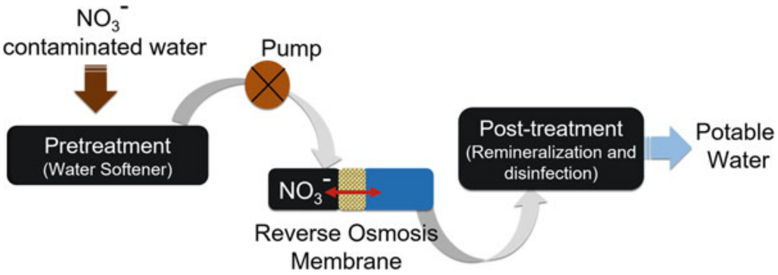


Fig. 6.10 Schematic illustration of reverse osmosis for removal of nitrate

In comparison with the nanofiltration process, reverse osmosis is operated under higher pressure and lower recovery efficiency. However, in the case studied by Häyrynen et al., the removal of nitrate using reverse osmosis setup was completely successful, while a poor separation performance toward nitrate was obtained by the nanofiltration membrane (Häyrynen et al. 2009). These results indicated that the efficiency of the membrane technology in the denitrification process can be varied based on the membrane type and the water quality (Tepuš et al. 2009).

To take the advantages of nanofiltration and reverse osmosis, the combined use of these technologies was proposed for selective removal of nitrate from groundwater (Epsztein et al. 2015) and production of high-quality water (Cartagena et al. 2013). The methodology of this system was based on the removal of chloride and sodium ions by the selective nanofiltration membranes to a side stream in a preliminary stage followed by nitrate removal in the reverse osmosis stage. After removal of nitrate, the side stream of nanofiltration step was mixed with the reverse osmosis permeate in order to create product water with a balanced composition of all required spices and minerals. The nitrate-rich brine of the reverse osmosis stage with low salinity can be used for irrigation purposes. This system also provided low concentrated waste brine and high recovery (Epsztein et al. 2015).

6.8 Nitrate Removal by Nanomaterial-Assisted Capacitive Deionization

Capacitive deionization technology is based on the electrostatic adsorption of ions onto the surface of charged electrodes under an applied electric field (0.7–1.5 V). This electro-sorption process could become a serious competitor with reverse osmosis for selective removal of nitrate from the wastewater stream. Carbon-based materials due to their porous structure, large specific surface area, high wettability, and excellent electrical conductivity have been extensively used as an electrode in this system (Oren 2008). In the capacitive deionization technology, wastewater containing nitrate and other ions flow through a pair of porous electrodes with opposite charges. As a result, the positively charged ions are captured by the negative electrode, while the negatively charged ions are separated from the solution at the positive electrode. After a time of operation, the electrodes will be saturated by the waste ions, and thus regeneration of the electrodes is performed by applying a reverse potential or zero voltage, which leads to the desorption of ions into a waste container.

In order to improve the attraction of ions during the removal process as well as to decrease the required time for the regeneration of the electrodes, an asymmetric electrochemical capacitive deionization was proposed. In this approach, the surfaces of the carbon electrodes were covered with a nanoporous thin film of different metal oxide nanoparticles (SiO_2 and Al_2O_3) that have an inherent and opposite surface potential. This modification not only presented a unique possibility for faster regeneration of the electrodes but also increased the removal rates of nitrate (Leonard et al. 2009). In a similar approach, Lado et al. reported that coating of the carbon electrodes with different metal oxides reduces the electrodes' hydrophobicity and also increases the surface area of the electrodes. Therefore, faster ion transport through the carbon electrodes and higher adsorption site were achieved that improved the nitrate removal capacity of the electrodes (Lado et al. 2017).

As contaminated waters mostly contain a mixture of various ions (e.g., NO_3^-, Cl^-, F^-, Na^+, Fe^{3+}, Ca^{2+}), their desalination using captive deionization technology leads to the separation of all their cationic and anionic ions along with nitrate ions. However, most of these ions are not required to be removed from the contaminated water, and thus this separation method consumes unnecessary energy. A possible solution to overcome this problem is to cover the surface of carbon electrode with mesoporous ion exchange resin (pore size about 50–100 nm) with a high selectivity toward nitrate ions (Kim and Choi 2012; Yeo and Choi 2013). This strategy increases the throughput per unit size of the electrodes and significantly reduces the energy cost.

Although capacitive deionization is a promising approach for the selective removal of nitrate from contaminated water, the concentrated nitrate at the surface of the electrode needs to be further treated into nitrogen gas in order to prevent the discharge of separated nitrate to the environment. Moreover, this treatment can regenerate the electrode surface for further use. For this purpose, a Pd/NiAl-layered metal oxide film electrode (Pd nanoparticles on NiAl nanosheets) was prepared and replaced by the common carbon electrodes for electro-sorption/reduction of nitrate. Decorating of NiAl nanosheets with Pd nanoparticles creates loose porous nanostructures for nitrate electro-sorption followed by the catalytic denitrification process (Fig. 6.11) (Hu et al. 2018).

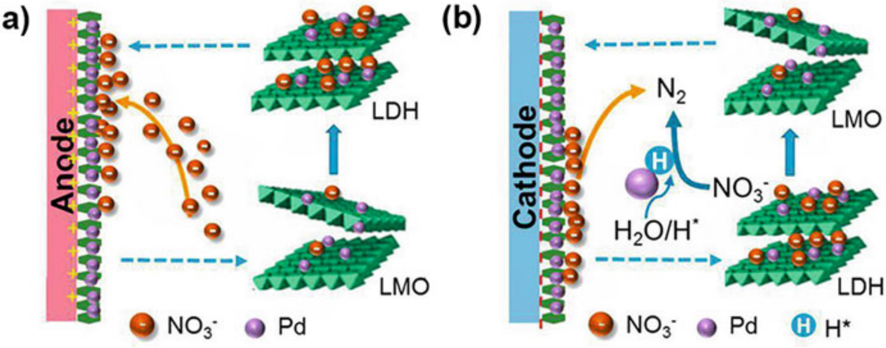


Fig. 6.11 Schematic illustration of (**a**) nitrate electro-sorption and (**b**) nitrate electro-reduction by the Pd/NiAl electrodes. LMO and LDH stand for the layered metal oxide and layered double hydroxides, respectively. (Reprinted with permission from Hu et al. 2018)

6.9 Patents Reported on the Removal of Nitrate by Nanomaterial Structures

To the best of our knowledge, there are only a few patents reported on nanomaterial-assisted technologies for denitrification processes. In this section, some of these inventions in connection with the use of metal oxide, adsorption, and membrane technologies for removal of nitrate from contaminated water are presented.

As discussed earlier, metal oxide nanoparticles such as zero-valent iron oxide have shown promising activities toward the removal of trace inorganic contaminants such as nitrate ions from water. However, packing of these nanomaterials into a standard column as a filter would result in channeling and high-pressure drop in the system. To overcome the undesirable pressure drop, US patent 20130206700 describes the design and development of a radial flow column including zero-valent iron particle (Gudipati and Woodling 2013).

US patent 20070256985 describes a method for the preparation of highly stabilized zero-valent iron nanoparticles in a liquid carrier. This method employs a composition containing select polysaccharides (starch or cellulose) as a stabilizer for the iron nanoparticles and facilitates the nanoparticles' dispersion and mobility for efficient removal of nitrate in the contaminated site (Zhao and Xu 2007).

US patent 20180086648 describes the use of aluminum hydr(oxide) nanoparticles in a porous hybrid media for removal of multiple contaminants (e.g., nitrate, fluoride) from contaminated water (Hristovski et al. 2018).

WO patent 2013126477 describes a method for removing nitrate ions from water stream using high-quality and low-cost biochar/metal nanocomposites. The nanocomposites were made of porous biochar phase and a metal phase (Mg, Al, Fe, Zn, or their combination) in the form of an oxide, a hydroxide, or an oxyhydroxide. The inventors also suggested that some of the exhausted biochar/metal composites (e.g., nutrient-loaded biochar/metal composites) can be reused as fertilizers to improve soil productivity (Gao et al. 2013).

WO patent 2005105272 describes a computer-designed nano-engineered membrane for separation of nitrate from water. The membrane has a nanopore structure with optimized sizes that preferentially pass nitrate ions into the waste stream, while it holds other ions with the water stream. Indeed, when the water stream is in contact with the membrane, the nanopores will be in a condition of double layer overlap and allow passage only of ions opposite to the electrical charge across the membrane (Wilson et al. 2005).

6.10 Summary and Outlook

Nitrate removal from contaminated water is one of the major engineering challenges due to the deep impact of this compound on human health and the ecological system. Therefore, several water treatment technologies have been developed to deal with this concern. In this context, nanotechnology has shown a tremendous influence on the optimization and improvement of these denitrification processes. Aside from all the advantages of these methods in the removal of nitrate from water, there are still some drawbacks that affect the efficiency and performance of these processes (Table 6.1). The separation-based technologies for removal of nitrate are mostly simple, convenient, easy to operate, and flexible in design. However, these technologies require significant posttreatment processes to avoid the disposal of separated contaminants to the environment. In comparison, the degradation-based technologies are capable of reducing the nitrate to innocuous nitrogen gas, though there are some problems (controlling the solution pH and temperature and providing efficient light source) associated with the operation of these technologies in the real world. Therefore, more investigation and efforts are required in order to develop a facile, fast, safe, cost-effective, and environmentally friendly technology for the efficient removal of nitrate from contaminated water.

Table 6.1 Comparison of different technologies used to remove nitrate

Method		Advantages	Disadvantages
Degradation-based technology	Chemical reduction using NZVI	High selectivity toward harmless products is possible (Liu et al. 2014a)	Production of by-product demands posttreatment
		Recovery of water is high (Jensen et al. 2012)	Effect of temperature and pH is important
			Stability of NZVI is low (Liu et al. 2014a)
	Catalytic denitrification	Efficiency is high (Hamid et al. 2015)	Stability of catalysts is low under specific conditions
		High selectivity toward harmless products is possible	
		A relatively mild condition is required (Hamid et al. 2015)	
	Photocatalytic denitrification	High selectivity toward harmless products is possible	Irradiation is required
		Can be installed in remote locations (Anderson 2011)	Effects of temperature and pH are important
	Biological denitrification	Multiple contaminants can be removed	Disposal of biomass wastes is required
		Recovery of water is high (Jensen et al. 2012)	Initial start-up is slow
			Effect of temperature and pH is important
		High selectivity toward harmless products (Bhatnagar and Sillanpää 2011)	Microorganisms in the product water require posttreatment (Bhatnagar and Sillanpää 2011)
Separation-based technologies	Adsorption	The operation is fast and easy (Bhatnagar and Sillanpää 2011)	Regeneration of the sorbent is required
			Effect of temperature and pH is important (Bhatnagar and Sillanpää 2011)
	Ion exchange	Selective removal of nitrate is possible	Regeneration of the resin is required
		Multiple contaminants can be removed (Jensen et al. 2012)	Resin fouling may occur
			pH adjustment is required to avoid corrosion
		Effects of temperature can be overlooked (Bhatnagar and Sillanpää 2011)	Disposal of waste brine is problematic (Bhatnagar and Sillanpää 2011)
	Electrodialysis	The lifetime of the membrane is high	Regeneration of the membrane is required
		Removal rate is controlled through voltage control	Applying potential is required
		Removal of multiple contaminants is possible (Jensen et al. 2012)	Disposal of waste concentrate is problematic (Jensen et al. 2012)

(continued)

Table 6.1 (continued)

Method		Advantages	Disadvantages
	Nanofiltration	Low energy is consumed (Santafé-Moros et al. 2007)	Not suitable for multicomponent solutions (Sancho et al. 2016)
		Selective removal of nitrate is possible (Jensen et al. 2012)	Medium pressure is required
			Disposal of waste concentrate is problematic (Jensen et al. 2012)
	Reverse osmosis	High-quality water is produced	Regeneration of the membrane is required
		Multiple contaminants can be removed	High pressure is required
		Effects of temperature and pH can be overlooked (Bhatnagar and Sillanpää 2011)	Corrosivity of product water demands posttreatment (Bhatnagar and Sillanpää 2011)
			Disposal of waste concentrate is problematic (Jensen et al. 2012)
	Capacitive deionization	Less environmental pollution can be produced	Regeneration of the electrode is required
		Low energy is consumed (Yeo and Choi 2013)	Applying potential is required

Acknowledgments The authors gratefully acknowledge the National Elites Foundation of Iran and Shiraz University for supporting this project. The authors greatly appreciate Mr. Mahdi Mohsenzadeh for his assistance in this work.

References

Akple MS, Low J, Qin Z, Wageh S, Al-Ghamdi AA, Yu J, Liu S (2015) Nitrogen-doped TiO_2 microsheets with enhanced visible light photocatalytic activity for CO_2 reduction. Chin J Catal 36(12):2127–2134. https://doi.org/10.1016/S1872-2067(15)60989-5

An Y, Li T, Jin Z, Dong M, Xia H, Wang X (2010) Effect of bimetallic and polymer-coated Fe nanoparticles on biological denitrification. Bioresour Technol 101(24):9825–9828. https://doi.org/10.1016/j.biortech.2010.07.110

Anderson JA (2011) Photocatalytic nitrate reduction over Au/TiO_2. Catal Today 175(1):316–321. https://doi.org/10.1016/j.cattod.2011.04.009

Ansari SA, Khan MM, Ansari MO, Cho MH (2016) Nitrogen-doped titanium dioxide (N-doped TiO_2) for visible light photocatalysis. New J Chem 40(4):3000–3009. https://doi.org/10.1039/C5NJ03478G

Azadbakht P, Pourzamani H, Petroudy S, Bina B (2016) Removal of nitrate from aqueous solution using nanocrystalline cellulose. Int J Environ Health Eng 5(1):17–17. https://doi.org/10.4103/2277-9183.190643

Babaei AA, Azari A, Rezaei Kalantary R, Kakavandi B (2015) Enhanced removal of nitrate from water using nZVI@MWCNTs composite: synthesis, kinetics and mechanism of reduction. Water Sci Technol 72(11):1988–1999. https://doi.org/10.2166/wst.2015.417

Bae S, Hanna K (2015) Reactivity of nanoscale zero-valent iron in unbuffered systems: effect of pH and Fe(II) dissolution. Environ Sci Technol 49(17):10536–10543. https://doi.org/10.1021/acs.est.5b01298

Barrabés N, Sá J (2011) Catalytic nitrate removal from water, past, present and future perspectives. Appl Catal B 104(1):1–5. https://doi.org/10.1016/j.apcatb.2011.03.011

Beiki MR, Yazdian F, Rasekh B, Rashedi H, Rostami AD (2016) Effect of metal nanoparticles on biological denitrification process: a review. J Appl Biotechnol Rep 3(1):353–358

Bekhradinassab E, Sabbaghi S (2014) Removal of nitrate from drinking water using nano SiO_2–FeOOH–Fe core–shell. Desalination 347:1–9. https://doi.org/10.1016/j.desal.2014.05.024

Bhatnagar A, Sillanpää M (2011) A review of emerging adsorbents for nitrate removal from water. Chem Eng J 168(2):493–504. https://doi.org/10.1016/j.cej.2011.01.103

Bhatnagar A, Kumar E, Sillanpää M (2010) Nitrate removal from water by nano-alumina: characterization and sorption studies. Chem Eng J 163(3):317–323. https://doi.org/10.1016/j.cej.2010.08.008

Cai Y, Feng YP (2016) Review on charge transfer and chemical activity of TiO_2: mechanism and applications. Prog Surf Sci 91(4):183–202. https://doi.org/10.1016/j.progsurf.2016.11.001

Cartagena P, El Kaddouri M, Cases V, Trapote A, Prats D (2013) Reduction of emerging micropollutants, organic matter, nutrients and salinity from real wastewater by combined MBR-NF/RO treatment. Sep Purif Technol 110:132–143. https://doi.org/10.1016/j.seppur.2013.03.024

Chen D, Yang K, Wang H (2016) Effects of important factors on hydrogen-based autotrophic denitrification in a bioreactor. Desalin Water Treat 57(8):3482–3488. https://doi.org/10.1080/19443994.2014.986533

Chiueh PT, Lee YH, Su CY, Lo SL (2011) Assessing the environmental impact of five Pd-based catalytic technologies in removing of nitrates. 192:837–845. https://doi.org/10.1016/j.jhazmat.2011.05.096

David MB, Drinkwater LE, McIsaac GF (2010) Sources of nitrate yields in the Mississippi River Basin. J Environ Qual 39(5):1657–1667. https://doi.org/10.2134/jeq2010.0115

Dizge N (2014) Performance evaluation of cross-flow membrane system for wastewater reuse from the wood-panels industry. Environ Technol 35(6):681–690. https://doi.org/10.1080/09593330.2013.841293

Dong J, Zhao Y, Zhao R, Zhou R (2010) Effects of pH and particle size on kinetics of nitrobenzene reduction by zero-valent iron. J Environ Sci 22(11):1741–1747. https://doi.org/10.1016/S1001-0742(09)60314-4

Doudrick K, Yang T, Hristovski K, Westerhoff P (2013) Photocatalytic nitrate reduction in water: managing the hole scavenger and reaction by-product selectivity. Appl Catal B 136–137:40–47. https://doi.org/10.1016/j.apcatb.2013.01.042

Dozzi MV, Selli E (2013) Doping TiO_2 with p-block elements: effects on photocatalytic activity. J Photochem Photobiol C 14(Supplement C):13–28. https://doi.org/10.1016/j.jphotochemrev.2012.09.002

Epsztein R, Nir O, Lahav O, Green M (2015) Selective nitrate removal from groundwater using a hybrid nanofiltration–reverse osmosis filtration scheme. Chem Eng J 279:372–378. https://doi.org/10.1016/j.cej.2015.05.010

Fu F, Dionysiou DD, Liu H (2014) The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. J Hazard Mater 267(Supplement C):194–205. https://doi.org/10.1016/j.jhazmat.2013.12.062

Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. Nature 238(5358):37–38. https://doi.org/10.1038/238037a0

Gao B, Zhang M, Yao Y (2013) Biochar/metal composites, methods of making biochar/metal composites, and methods of removing contaminants from water. WO Patent 2013126477

Garcia Segura S, Brillas E (2017) Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters. J Photochem Photobiol C 31(Supplement C):1–35. https://doi.org/10.1016/j.jphotochemrev.2017.01.005

Geiger CL, Ruiz NE, Clausen CA, Reinhart DR, Quinn JW (2002) Ultrasound pretreatment of elemental iron: kinetic studies of dehalogenation reaction enhancement and surface effects. Water Res 36(5):1342–1350. https://doi.org/10.1016/S0043-1354(01)00319-0

Ghaee A, Zerafat MM, Askari P, Sabbaghi S, Sadatnia B (2017) Fabrication of polyamide thin-film nanocomposite membranes with enhanced surface charge for nitrate ion removal from water resources. Environ Technol 38(6):772–781. https://doi.org/10.1080/09593330.2016.1231223

Gheju M (2011) Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems. Water Air Soil Pollut 222(1):103–148. https://doi.org/10.1007/s11270-011-0812-y

Girish Kumar S, Koteswara Rao KSR (2015) Tungsten-based nanomaterials (WO_3 & Bi_2WO_6): modifications related to charge carrier transfer mechanisms and photocatalytic applications. Appl Surf Sci 355(Supplement C):939–958. https://doi.org/10.1016/j.apsusc.2015.07.003

Guan X, Sun Y, Qin H, Li J, Lo IMC, He D, Dong H (2015) The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: the development in zero-valent iron technology in the last two decades (1994–2014). Water Res 75(Supplement C):224–248. https://doi.org/10.1016/j.watres.2015.02.034

Gudipati CS, Woodling RE (2013) Radial flow column including zero-valent iron media. US Patent 20130206700, 15 Aug 2013

Gündüz O (2015) Water quality perspectives in a changing world. Water Qual Expo Health 7 (1):1–3. https://doi.org/10.1007/s12403-015-0161-y

Hamid S, Bae S, Lee W, Amin MT, Alazba AA (2015) Catalytic nitrate removal in continuous bimetallic Cu–Pd/nanoscale zerovalent iron system. Ind Eng Chem Res 54(24):6247–6257. https://doi.org/10.1021/acs.iecr.5b01127

Harris TD, Smith VH, Graham JL, Van de Waal DB, Tedesco LP, Clercin N (2016) Combined effects of nitrogen to phosphorus and nitrate to ammonia ratios on cyanobacterial metabolite concentrations in eutrophic Midwestern USA reservoirs. Inland Waters 6(2):199–210. https://doi.org/10.5268/IW-6.2.938

Häyrynen K, Pongrácz E, Väisänen V, Pap N, Mänttäri M, Langwaldt J, Keiski RL (2009) Concentration of ammonium and nitrate from mine water by reverse osmosis and nanofiltration. Desalination 240(1–3):280–289. https://doi.org/10.1016/j.desal.2008.02.027

Hoinkis J, Valero-Freitag S, Caporgno MP, Pätzold C (2011) Removal of nitrate and fluoride by nanofiltration – a comparative study. Desalin Water Treat 30(1–3):278–288. https://doi.org/10.5004/dwt.2011.2103

Hord NG, Conley MN (2017) Regulation of dietary nitrate and nitrite: balancing essential physiological roles with potential health risks. In: Bryan NS, Loscalzo J (eds) Nitrite and nitrate in human health and disease. Humana Press, Cham, pp 153–162. https://doi.org/10.1007/978-3-319-46189-2

Hosseini SM, Ataie Ashtiani B, Kholghi M (2011) Nitrate reduction by nano-Fe/Cu particles in packed column. Desalination 276(1):214–221. https://doi.org/10.1016/j.desal.2011.03.051

Hristovski KD, Markovski J, Westerhoff PK, Sinha S (2018) Low temperature synthesis of aluminum hydr(oxide) inside porous media. US Patent 20180086648, 29 Mar 2018

Hu C, Dong J, Wang T, Liu R, Liu H, Qu J (2018) Nitrate electro-sorption/reduction in capacitive deionization using a novel Pd/NiAl-layered metal oxide film electrode. Chem Eng J 335 (Supplement C):475–482. https://doi.org/10.1016/j.cej.2017.10.167

Hwang YH, Kim DG, Shin HS (2011) Effects of synthesis conditions on the characteristics and reactivity of nano scale zero valent iron. Appl Catal B 105(1):144–150. https://doi.org/10.1016/j.apcatb.2011.04.005

Im JK, Son HS, Zoh KD (2011) Perchlorate removal in Fe^0/H_2O systems: impact of oxygen availability and UV radiation. J Hazard Mater 192(2):457–464. https://doi.org/10.1016/j.jhazmat.2011.05.030

Jamei MR, Khosravi MR, Anvaripour B (2013) Investigation of ultrasonic effect on synthesis of nano zero valent iron particles and comparison with conventional method. Asia Pac J Chem Eng 8(5):767–774. https://doi.org/10.1002/apj.1720

Jensen VB, Darby JL, Seidel C, Gorman C (2012) Drinking water treatment for nitrate. Technical report 6 in: addressing nitrate in California's drinking water with a focus on Tulare lake basin and Salinas valley groundwater. Report for the state water resources control board report to the legislature. Center for Watershed Sciences, University of California, Davis

Jiang C, Liu Y, Chen Z, Megharaj M, Naidu R (2013) Impact of iron-based nanoparticles on microbial denitrification by Paracoccus sp. strain YF1. Aquat Toxicol 142–143:329–335. https://doi.org/10.1016/j.aquatox.2013.09.005

Juholin P, Kääriäinen ML, Riihimäki M, Sliz R, Aguirre JL, Pirilä M, Fabritius T, Cameron D, Keiski RL (2018) Comparison of ALD coated nanofiltration membranes to unmodified commercial membranes in mine wastewater treatment. Sep Purif Technol 192:69–77. https://doi.org/10.1016/j.seppur.2017.09.005

Jung J, Bae S, Lee W (2012) Nitrate reduction by maghemite supported Cu-Pd bimetallic catalyst. Appl Catal B Environ 127(Supplement C):148–158. https://doi.org/10.1016/j.apcatb.2012.08.017

Khalil AME, Eljamal O, Jribi S, Matsunaga N (2016) Promoting nitrate reduction kinetics by nanoscale zero valent iron in water via copper salt addition. Chem Eng J 287:367–380. https://doi.org/10.1016/j.cej.2015.11.038

Khalil AME, Eljamal O, Amen TWM, Sugihara Y, Matsunaga N (2017a) Optimized nano-scale zero-valent iron supported on treated activated carbon for enhanced nitrate and phosphate removal from water. Chem Eng J 309(Supplement C):349–365. https://doi.org/10.1016/j.cej.2016.10.080

Khalil AME, Eljamal O, Eljamal R, Sugihara Y, Matsunaga N (2017b) Treatment and regeneration of nano-scale zero-valent iron spent in water remediation. Evergreen 4(1):21–28

Kim YJ, Choi JH (2012) Selective removal of nitrate ion using a novel composite carbon electrode in capacitive deionization. Water Res 46(18):6033–6039. https://doi.org/10.1016/j.watres.2012.08.031

Kim DG, Hwang YH, Shin HS, Ko SO (2013) Deactivation of nanoscale zero-valent iron by humic acid and by retention in water. Environ Technol 34(12):1625–1635. https://doi.org/10.1080/09593330.2013.765916

Kobwittaya K, Sirivithayapakorn S (2014) Photocatalytic reduction of nitrate over TiO_2 and Ag-modified TiO_2. J Saudi Chem Soc 18(4):291–298. https://doi.org/10.1016/j.jscs.2014.02.001

Kochuveedu ST, Jang YH, Kim DH (2013) A study on the mechanism for the interaction of light with noble metal-metal oxide semiconductor nanostructures for various photophysical applications. Chem Soc Rev 42(21):8467–8493. https://doi.org/10.1039/C3CS60043B

Lado JJ, Pérez Roa RE, Wouters JJ, Tejedor Tejedor MI, Federspill C, Ortiz JM, Anderson MA (2017) Removal of nitrate by asymmetric capacitive deionization. Sep Purif Technol 183 (Supplement C):145–152. https://doi.org/10.1016/j.seppur.2017.03.071

Leonard KC, Genthe JR, Sanfilippo JL, Zeltner WA, Anderson MA (2009) Synthesis and characterization of asymmetric electrochemical capacitive deionization materials using nanoporous silicon dioxide and magnesium doped aluminum oxide. Electrochim Acta 54(22):5286–5291. https://doi.org/10.1016/j.electacta.2009.01.082

Li P, Lin K, Fang Z, Wang K (2017) Enhanced nitrate removal by novel bimetallic Fe/Ni nanoparticles supported on biochar. J Clean Prod 151(Supplement C):21–33. https://doi.org/10.1016/j.jclepro.2017.03.042

Liou YH, Lo SL, Lin CJ, Kuan WH, Weng SC (2005) Effects of iron surface pretreatment on kinetics of aqueous nitrate reduction. J Hazard Mater 126(1):189–194. https://doi.org/10.1016/j.jhazmat.2005.06.038

Liu HB, Chen TH, Chang DY, Chen D, Liu Y, He HP, Yuan P, Frost R (2012) Nitrate reduction over nanoscale zero-valent iron prepared by hydrogen reduction of goethite. Mater Chem Phys 133(1):205–211. https://doi.org/10.1016/j.matchemphys.2012.01.008

Liu H, Guo M, Zhang Y (2014a) Nitrate removal by Fe^0/Pd/Cu nano-composite in groundwater. Environ Technol 35(7):917–924. https://doi.org/10.1080/09593330.2013.856926

Liu XW, Li WW, Yu HQ (2014b) Cathodic catalysts in bioelectrochemical systems for energy recovery from wastewater. Chem Soc Rev 43(22):7718–7745. https://doi.org/10.1039/C3CS60130G

Liu Y, Lee J, Zhao Y, Zhang M, Wang L, Duan Q (2014c) A novel preparation approach and denitrification performance of TiO_2/Fe^0 photocatalysts. Desalin Water Treat 57(7):3125–3131. https://doi.org/10.1080/19443994.2014.983984

Liu Y, Li S, Chen Z, Megharaj M, Naidu R (2014d) Influence of zero-valent iron nanoparticles on nitrate removal by Paracoccus sp. Chemosphere 108(Supplement C):426–432. https://doi.org/10.1016/j.chemosphere.2014.02.045

Lozovskii AV, Stolyarova IV, Prikhod'ko RV, Goncharuk VV (2009) Research of photocatalytic activity of the Ag/TiO_2 catalysts in the reduction reaction of nitrate-ions in aqueous media. J Water Chem Technol 31(6):360–366. https://doi.org/10.3103/S1063455X09060034

Luiz DDB, Andersen SLF, Berger C, José HJ, Moreira RDFPM (2012) Photocatalytic reduction of nitrate ions in water over metal-modified TiO_2. J Photochem Photobiol A 246(Supplement C):36–44. https://doi.org/10.1016/j.jphotochem.2012.07.011

Malaeb L, Ayoub GM (2011) Reverse osmosis technology for water treatment: state of the art review. Desalination 267:1–8. https://doi.org/10.1016/j.desal.2010.09.001

Matatov-Meytal U, Sheintuch M (2005) Activated carbon cloth-supported Pd–cu catalyst: application for continuous water denitrification. Catal Today 102:121–127. https://doi.org/10.1016/j.cattod.2005.02.015

Markovski J, Garcia J, Hristovski KD, Westerhoff P (2017) Nano-enabling of strong-base ion-exchange media via a room-temperature aluminum (hydr)oxide synthesis method to simultaneously remove nitrate and fluoride. Sci Total Environ 599–600:1848–1855. https://doi.org/10.1016/j.scitotenv.2017.05.083

Mautner A, Maples HA, Sehaqui H, Zimmermann T, Perez De Larraya U, Mathew AP, Lai CY, Li K, Bismarck A (2016) Nitrate removal from water using a nanopaper ion-exchanger. Environ Sci Water Res Technol 2(1):117–124. https://doi.org/10.1039/c5ew00139k

Mook WT, Aroua MK, Chakrabarti MH, Low CTJ, Aravind PV, Brandon NP (2013) The application of nano-crystalline PbO2 as an anode for the simultaneous bio-electrochemical denitrification and organic matter removal in an up-flow undivided reactor. Electrochim Acta 94:327–335. https://doi.org/10.1016/j.electacta.2013.02.001

Ni S-Q, Ni J, Yang N, Wang J (2013) Effect of magnetic nanoparticles on the performance of activated sludge treatment system. Bioresour Technol 143(Supplement C):555–561. https://doi.org/10.1016/j.biortech.2013.06.041

O'Carroll D, Sleep B, Krol M, Boparai H, Kocur C (2013) Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. Adv Water Resour 51(Supplement C):104–122. https://doi.org/10.1016/j.advwatres.2012.02.005

Oren Y (2008) Capacitive deionization (CDI) for desalination and water treatment – past, present and future (a review). Desalination 228(1):10–29. https://doi.org/10.1016/j.desal.2007.08.005

Pan JR, Huang C, Hsieh WP, Wu BJ (2012) Reductive catalysis of novel TiO_2/Fe^0 composite under UV irradiation for nitrate removal from aqueous solution. Sep Purif Technol 84(Supplement C):52–55. https://doi.org/10.1016/j.seppur.2011.06.024

Paschoal FMM, Nuñez L, Lanza MRDV, Zanoni MVB (2013) Nitrate removal on a Cu/Cu_2O photocathode under UV irradiation and bias potential. J Adv Oxid Technol 16(1):63–70. https://doi.org/10.1515/jaots-2013-0106

Peng L, Liu Y, Gao SH, Chen X, Xin P, Dai X, Ni BJ (2015) Evaluation on the nanoscale zero valent iron based microbial denitrification for nitrate removal from groundwater. Sci Rep 5 (1):12331. https://doi.org/10.1038/srep12331

Pintar A, Batista J, Levec J (2001) Integrated ion exchange/catalytic process for efficient removal of nitrates from drinking water. Chem Eng Sci 56(4):1551–1559. https://doi.org/10.1016/S0009-2509(00)00382-1

Ranjit KT, Viswanathan B (1997) Photocatalytic reduction of nitrite and nitrate ions over doped TiO_2 catalysts. J Photochem Photobiol A 107(1):215–220. https://doi.org/10.1016/S1010-6030(97)00025-7

Reig M, Licon E, Gibert O, Yaroshchuk A, Cortina JL (2016) Rejection of ammonium and nitrate from sodium chloride solutions by nanofiltration: effect of dominant-salt concentration on the trace-ion rejection. Chem Eng J 303:401–408. https://doi.org/10.1016/j.cej.2016.06.025

Ren HT, Jia SY, Zou JJ, Wu SH, Han X (2015) A facile preparation of Ag_2O/P25 photocatalyst for selective reduction of nitrate. Appl Catal B 176–177(Supplement C):53–61. https://doi.org/10.1016/j.apcatb.2015.03.038

Richards LA, Vuachère M, Schäfer AI (2010) Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis. Desalination 261(3):331–337. https://doi.org/10.1016/j.desal.2010.06.025

Sá J, Agüera CA, Gross S, Anderson JA (2009) Photocatalytic nitrate reduction over metal modified TiO_2. Appl Catal B 85(3):192–200. https://doi.org/10.1016/j.apcatb.2008.07.014

Sá J, Barrabes N, Kleymenov E, Lin C, Föttinger K, Safonova OV, Szlachetko J, van Bokhoven JA, Nachtegaal M, Urakawa A, Crespo GA, Rupprechter G (2012) The oxidation state of copper in bimetallic (Pt-Cu, Pd-Cu) catalysts during water denitration. Cat Sci Technol 2(4):794–799. https://doi.org/10.1039/C2CY00461E

Sancho M, Álvarez Blanco S, Kombo GOM, García Fayos B (2016) Experimental determination of nanofiltration models: application to nitrate removal. Desalin Water Treat 57 (48–49):22852–22859. https://doi.org/10.1080/19443994.2016.1173380

Santafé-Moros A, Gozálvez-Zafrilla JM, Lora-García J (2007) Nitrate removal from ternary ionic solutions by a tight nanofiltration membrane. Desalination 204(1):63–71. https://doi.org/10.1016/j.desal.2006.04.024

Shi J, Yi S, He H, Long C, Li A (2013) Preparation of nanoscale zero-valent iron supported on chelating resin with nitrogen donor atoms for simultaneous reduction of Pb^{2+} and NO_3. Chem Eng J 230(Supplement C):166–171. https://doi.org/10.1016/j.cej.2013.06.088

Shimizu A, Tokumura M, Nakajima K, Kawase Y (2012) Phenol removal using zero-valent iron powder in the presence of dissolved oxygen: roles of decomposition by the Fenton reaction and adsorption/precipitation. J Hazard Mater 201–202(Supplement C):60–67. https://doi.org/10.1016/j.jhazmat.2011.11.009

Shin H, Jung S, Bae S, Lee W, Kim H (2014) Nitrite reduction mechanism on a Pd surface. Environ Sci Technol 48(21):12768–12774. https://doi.org/10.1021/es503772x

Shinde SS, Bhosale CH, Rajpure KY (2011) Photocatalytic activity of sea water using TiO_2 catalyst under solar light. J Photochem Photobiol B 103(2):111–117. https://doi.org/10.1016/j.jphotobiol.2011.02.002

Su Y, Adeleye AS, Huang Y, Sun X, Dai C, Zhou X, Zhang Y, Keller AA (2014) Simultaneous removal of cadmium and nitrate in aqueous media by nanoscale zerovalent iron (nZVI) and Au doped nZVI particles. Water Res 63(Supplement C):102–111. https://doi.org/10.1016/j.watres.2014.06.008

Sun D, Yang J, Li J, Yu J, Xu X, Yang X (2010) Novel Pd-Cu/bacterial cellulose nanofibers: preparation and excellent performance in catalytic denitrification. Appl Surf Sci 256 (7):2241–2244. https://doi.org/10.1016/j.apsusc.2009.10.034

Sun D, Yang W, Zhou L, Sun W, Li Q, Shang JK (2016a) The selective deposition of silver nanoparticles onto {101} facets of TiO_2 nanocrystals with co-exposed {001}/{101} facets, and their enhanced photocatalytic reduction of aqueous nitrate under simulated solar illumination. Appl Catal B 182(Supplement C):85–93. https://doi.org/10.1016/j.apcatb.2015.09.005

Sun W, Li Q, Gao S, Shang JK (2012) Monometallic Pd/Fe_3O_4 catalyst for denitrification of water. Appl Catal B 125:1–9. https://doi.org/10.1016/j.apcatb.2012.05.014

Sun Y, Li J, Huang T, Guan X (2016b) The influences of iron characteristics, operating conditions and solution chemistry on contaminants removal by zero-valent iron: a review. Water Res 100 (Supplement C):277–295. https://doi.org/10.1016/j.watres.2016.05.031

Suzuki T, Moribe M, Oyama Y, Niinae M (2012) Mechanism of nitrate reduction by zero-valent iron: equilibrium and kinetics studies. Chem Eng J 183:271–277. https://doi.org/10.1016/j.cej.2011.12.074

Tacke T, Vorlop KD (1993) Kinetische charakterisierung von katalysatoren zur selektiven entfernung von nitrat und nitrit aus wasser. Chem Ing Tech 65:1500–1502. https://doi.org/10.1002/cite.330651216

Tang C, Zhang Z, Sun X (2012) Effect of common ions on nitrate removal by zero-valent iron from alkaline soil. J Hazard Mater 231–232(Supplement C):114–119. https://doi.org/10.1016/j.jhazmat.2012.06.042

Tang S, Wang XM, Mao YQ, Zhao Y, Yang HW, Xie YF (2015) Effect of dissolved oxygen concentration on iron efficiency: removal of three chloroacetic acids. Water Res 73(Supplement C):342–352. https://doi.org/10.1016/j.watres.2015.01.027

Tepuš B, Simonič M, Petrinić I (2009) Comparison between nitrate and pesticide removal from ground water using adsorbents and NF and RO membranes. J Hazard Mater 170 (2–3):1210–1217. https://doi.org/10.1016/j.jhazmat.2009.05.105

Tugaoen HON, Garcia-Segura S, Hristovski K, Westerhoff P (2017) Challenges in photocatalytic reduction of nitrate as a water treatment technology. Sci Total Environ 599–600:1524–1551. https://doi.org/10.1016/j.scitotenv.2017.04.238

Tung RT (2014) The physics and chemistry of the schottky barrier height. Appl Phys Rev 1:1–54. https://doi.org/10.1063/1.4858400

Vaselbehagh M, Karkhanechi H, Takagi R, Matsuyama H (2015) Surface modification of an anion exchange membrane to improve the selectivity for monovalent anions in electrodialysis – experimental verification of theoretical predictions. J Membr Sci 490:301–310. https://doi.org/10.1016/j.memsci.2015.04.014

Wang H, Turner JA (2013) Photoelectrochemical reduction of nitrates at the illuminated p-$GaInP_2$ photoelectrode. Energy Environ Sci 6(6):1802–1805. https://doi.org/10.1039/C3EE40745D

Wang KS, Lin CL, Wei MC, Liang HH, Li HC, Chang CH, Fang YT, Chang SH (2010) Effects of dissolved oxygen on dye removal by zero-valent iron. J Hazard Mater 182(1):886–895. https://doi.org/10.1016/j.jhazmat.2010.07.002

Wehbe N, Jaafar M, Guillard C, Herrmann JM, Miachon S, Puzenat E, Guilhaume N (2009) Comparative study of photocatalytic and non-photocatalytic reduction of nitrates in water. Appl Catal A 368(1):1–8. https://doi.org/10.1016/j.apcata.2009.07.038

Wilson WD, Schaldach CM, Bourcier WL, Paul PH (2005) Smart membranes for nitrate removal, water purification, and selective ion transportation. WO Patent 2005105272, 10 Sep 2005

Wisniewski C, Persin F, Cherif T, Sandeaux R, Grasmick A, Gavach C, Lutin F (2002) Use of a membrane bioreactor for denitrification of brine from an electrodialysis process. Desalination 149:331–336. https://doi.org/10.1016/S0011-9164(02)00805-6

Wu D, You H, Liu W, Du J, Jin D (2009) Preparation and photocatalytic bactericidal activity of silver loaded TiO_2 thin films. Huagong Xuebao 60(7):1693–1699

Yeo JH, Choi JH (2013) Enhancement of nitrate removal from a solution of mixed nitrate, chloride and sulfate ions using a nitrate-selective carbon electrode. Desalination 320(Supplement C):10–16. https://doi.org/10.1016/j.desal.2013.04.013

Yin W, Wu J, Li P, Wang X, Zhu N, Wu P, Yang B (2012) Experimental study of zero-valent iron induced nitrobenzene reduction in groundwater: the effects of pH, iron dosage, oxygen and common dissolved anions. Chem Eng J 184(Supplement C):198–204. https://doi.org/10.1016/j.cej.2012.01.030

Yoon IH, Bang S, Chang JS, Gyu Kim M, Kim KW (2011) Effects of pH and dissolved oxygen on Cr(VI) removal in Fe(0)/H_2O systems. J Hazard Mater 186(1):855–862. https://doi.org/10.1016/j.jhazmat.2010.11.074

Zeng Y, Walker H, Zhu Q (2017) Reduction of nitrate by NaY zeolite supported Fe, Cu/Fe and Mn/Fe nanoparticles. J Hazard Mater 324(Part B):605–616. https://doi.org/10.1016/j.jhazmat.2016.11.032

Zhang Y, Li Y, Li J, Hu L, Zheng X (2011) Enhanced removal of nitrate by a novel composite: nanoscale zero valent iron supported on pillared clay. Chem Eng J 171(2):526–531. https://doi.org/10.1016/j.cej.2011.04.022

Zhao D, Xu Y (2007) In situ remediation of inorganic contaminants using stabilized zero-valent iron nanoparticles. US Patent 20070256985, 8 Nov 2007

Zhu I, Getting T (2012) A review of nitrate reduction using inorganic materials. Environ Technol Rev 1(1):46–58. https://doi.org/10.1080/09593330.2012.706646

Chapter 7
Nanoencapsulation of Food Carotenoids

D. H. Lohith Kumar, Jayeeta Mitra, and S. S. Roopa

Contents

7.1 Introduction 204
7.2 Nanoencapsulation Matrices for Carotenoids 205
  7.2.1 Liquid Matrices 206
  7.2.2 Solid Matrices 216
  7.2.3 Semisolid Matrices 218
7.3 Nanopatterning of Different Encapsulation Matrices 219
  7.3.1 Patterning Based on Size Reduction 219
  7.3.2 Patterning Based on Surface Functionalization 223
7.4 Designing Food Matrices for Nanoencapsulated Carotenoids: Role of Excipients in Protection of Carotenoids in the GI Tract 227
7.5 Factors Affecting Nanoencapsulation of Carotenoids 230
7.6 Bioavailability of Encapsulated Carotenoids: Influence of Structural Barriers, Food Structure, and Dietary Factors 231
7.7 Co-encapsulation of Carotenoids with Other Functional Ingredients 234
7.8 Conclusion 235
References 235

Abstract There is an increasing demand for delivery of carotenoids through functional foods with the concomitant challenge of protecting their bioactivity during different food unit operations and subsequent passage through the gastrointestinal tract. Evolving evidence on the health benefits of carotenoids has sparked interest in nanoencapsulation and utilization of encapsulation matrices in food fortification. Different nanoencapsulation matrices such as emulsions, nanoparticles, liposomes, hydrogels, clusters, and nanocrystals demonstrated compatibility with different food

---

D. H. Lohith Kumar
Bioprocess Engineering Laboratory, Department of Biotechnology, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand, India

J. Mitra (✉)
Department of Agricultural and Food Engineering, Indian Institute of Technology, Kharagpur, West Bengal, India

S. S. Roopa
Britannia Industries Limited, Ramanagara, Karnataka, India

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_7

matrices. In addition, nanoencapsulation matrix could be designed to help decrease the degradation of the carotenoids. This chapter reviews the aspects of carotenoid nanoencapsulation and their bioavailability in food matrices. Additionally, co-encapsulation strategies to enhance bioavailability and bioaccessibility are discussed.

Keywords Nanoencapsulation · Carotenoids · β-carotene · Nano-fortification · Nano-additives

7.1 Introduction

Carotenoids are naturally occurring colored pigments with unique structural diversity and functionalities. Structurally carotenoids are tetra-terpenes formed from eight isoprene units, resulting in symmetrical molecules. The existence of π-electrons in centrally located conjugated double bonds is efficiently delocalized throughout the polyene chain. This alternative single and double bond system institutes the light-absorbing chromosphere which is responsible for the color and unique functionalities of carotenoids (Liaaen-Jensen and Jensen 1966). However, it also reduces the molecule prone to oxidative degradation and geometric isomerization (Havaux 2014). There is a huge demand for mixed carotenoids as it has surplus applications starting from medical to cosmetic field. The linkage of the carotenoids can be modified by chemical modifications such as cyclization, varying the hydrogenation level, and adding of functional groups with oxygen. These carotenoids are recognized for prevention of diseases which are caused due to oxidative stress like cancer and age-related diseases as there is no oxygen molecule attached to its functional group (Noviendri et al. 2011). In addition, certain lipophilic carotenoids provides vitamin property and finds many applications in micelle formation, colors in beverages and functional foods (Sarkar et al. 2015). As consumers switch for the natural or organic health benefits of food additives for the last decades, carotenoids are preferred mostly.

As a heterogeneous dispersion system, foods generally have a high content of amphiphilic compounds, among which the non-covalent and covalent interaction occurs, which is determined by different bonding forces in the food unit operations such as homogenization, heating, and frying. When carotenoids undergo through these different unit operations, often their functionality and bioavailability reduce. In addition, bioavailability of carotenoids is often reduced due to poor solubility, degradation during assimilation, and release patterns from the food matrix. Moreover, oxidative degradation of carotenoids reduces the nutritional value of food along with the development of off-flavor, discoloration, and lipid prooxidants. Therefore, conveying carotenoids to the human body via nanoencapsulation can enhance the bioavailability and release kinetics in food matrices (Qian et al. 2012b). Nanoencapsulation matrices are passive nanostructures employed to protect during processing and enhance the efficacy of functional compounds such as carotenoids, polyunsaturated fatty acids, antioxidants, and essential oils.

Nanoencapsulation technology is expanding rapidly with a number of potential applications in areas of food and pharmaceutical industry. An increasing number of studies have found that utilization of nanostructures in food supplements or foods requires suitable regulations to assess the toxicology and their potential for application. However, research related to carotenoid encapsulation is still very less compared to other bioactive compound encapsulation. This might be attributed to the fact that technical challenges are normally associated with incorporation of these active compounds into commercial food and beverage products. Nevertheless, there are examples for nanotechnology-based food products available in market such as LycoVit which is a nanoparticulate lycopene, a European product developed by BASF, which is claimed for use as food fortifying agent and supplement. In addition, this product has been categorized under generally recognized as safe by the US Food and Drug Administration (Faisal et al. 2010). In general, encapsulation systems can be classified as shell- and core-based encapsulation matrices that can be used for both lipophilic and hydrophilic functional molecules. However, an effective synergism between the encapsulation system and nutraceutical compound is currently acknowledged as a key factor to ensure therapeutic efficiency (Lohith Kumar and Sarkar 2017, 2018; Quintanilla-Carvajal et al. 2010). This review will discuss the different nanoencapsulation matrices and patterning them at nanoscale along with evaluating different structural and dietary barriers for the bioavailability of encapsulated carotenoids.

7.2 Nanoencapsulation Matrices for Carotenoids

To ensure that a designed encapsulation matrix is ideal for an active compound, better fundamental understanding of food encapsulation matrix interaction at molecular level and association with functional properties is necessary. For instance, the location of bioactive compounds such as either bound on the surface or encapsulated inside of the nanoencapsulation matrices defines the potency of functionality (Augustin and Hemar 2009; Augustin and Sanguansri 2015). Various nanoencapsulation matrices such as emulsion, liposome, lipid particles, and hydrogels have been used to protect carotenoids according to the prerequisites of their applications (Bustos-Garza et al. 2013; Gomes et al. 2017; Liu et al. 2015; Tan et al. 2014b; Zhang et al. 2016b). Biodegradable matrices are highly preferred as they deliver controlled release characteristics and biocompatibility with cells and tissues. Recent research findings on nanoencapsulation of food carotenoids to protect during processing and storage and the ways of increasing bioavailability are presented in this section. Surprisingly, understanding of the chemistry behind carotenoid degradation during processing and storage remains narrow and fragmentary. In general, carotenoid degradation pattern, including oxidation and geometric isomerization, is known (Boon et al. 2010). For better understanding, nanoencapsulation matrices are categorized as liquid matrices, solid matrices, and semisolid matrices.

7.2.1 *Liquid Matrices*

Nanoemulsion

Nanoemulsions are passive nanostructures comprising of two liquid phases separated by a thin amphiphilic interfacial membrane (Fig. 7.1). Encapsulation of carotenoids in nanoemulsions proves to be an efficient delivery system. Though microemulsions are also considered for encapsulation, nanoemulsions are preferred due to increased physical stability, high optical transparency, processability, and greater bioavailability (Dasgupta et al. 2016). The biochemical stability of carotenoids during storage and emulsification depends on droplet properties (zeta potential, interfacial layer composition, droplet size), emulsion composition (type of carotenoid, concentration of oil, surfactant properties, and presence of free radicals or oxygen scavengers), extrinsic conditions (oxygen, light, temperature), and intrinsic conditions (ionic strength, pH, droplet surface charge) (McClements and Rao 2011).

Bioavailability of carotenoids can be enhanced by ingesting with dietary fat as the digested products of fat form micelles, which are capable of solubilizing and transporting carotenoids to epithelium cells (Palafox-Carlos et al. 2011). Hence, it can be concluded that emulsion matrix may be an ideal delivery vehicle for formulation of carotenoid-rich functional foods. Lipophilic carotenoids can be entrapped inside the oil droplets of an emulsion and thus be protected by hydrophilic free radicals located at the interface. Nanoemulsions as delivery vehicles for carotenes with the aim of investigating properties, preparation methods, and digestion

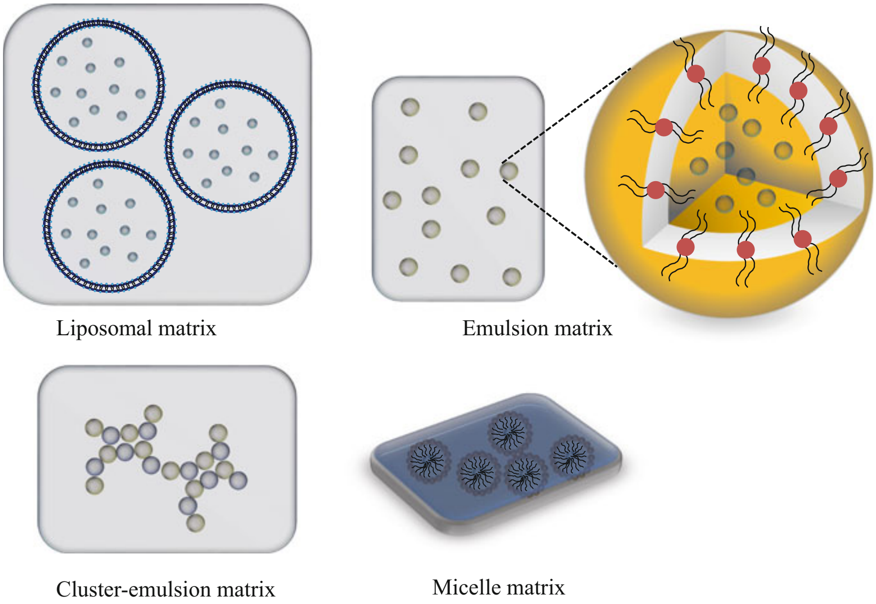


Fig. 7.1 Illustration of different liquid-based encapsulation matrices

behavior were studied intensively (Qian et al. 2012a, b, c; Rao et al. 2013; Yuan et al. 2008a). Among available nanoemulsion preparation techniques, high-pressure homogenization is the most used technique in both industries and laboratories as it allows producing different particle size ranges. It is observed that either increasing homogenization cycles or pressure results in saturation of droplet size reduction and wider distribution due to unchanged surface tension and emulsifier shortage at the interface. However, utilization of small molecular wright emulsifiers such as spans, tweens, polyglycerol esters of fatty acids, sugar esters instead of biopolymers such as milk proteins, and polysaccharides can help in obtaining smaller oil droplets.

In carotenoid nanoemulsion, emulsifier plays a critical role in physical, color, and chemical stability. Small molecular weight emulsifiers generally play a weak role in inhibiting carotene oxidation, probably because of the thin membrane formed at the oil-water interface; hence, surface-active biopolymers are preferred to produce carotene emulsions. It was observed in a study that nanoemulsion stabilized by sodium caseinate had larger particle size, but β-carotene had the best stability at 4 ° C for 8 weeks. When the blend of sodium caseinate and decaglycerol monolaurate is used as stabilizer, it enhanced the stability compared to decaglycerol monolaurate alone. However, the enhanced chemical stability might be attributed to the antioxidant property of casein at the interface (Yin et al. 2009). Similar findings were reported that emulsion formulated using β-lactoglobulin was more stable to discoloration than emulsion containing Tween 20 (Qian et al. 2012a). The different antioxidant effects of proteins could be associated with the different amino acid compositions and the interfacial structures in the emulsions. When different proteins were tested, sodium caseinate provided better protection than whey protein isolate against β-carotene degradation (Cornacchia and Roos 2011), and a mixture of Tween 20 and whey protein concentrate was capable of retaining more β-carotene than a mixture of Tween 20 and bovine serum albumin (Trentin et al. 2011).

In nanoemulsions, the carrier oil type largely affects the bioaccessibility of carotenoids. In general, long-chain triglycerides are a more effective carrier lipid phase compared to medium-chain triglycerides as they form enough mixed micelles during digestion and helps in solubilization of carotenoids (Qian et al. 2012b). The effect of oil composition on β-carotene bioavailability is influenced by preliminary total oil concentration. In low-fat emulsions, the bioavailability of bioactive compounds enhances progressively with increase in long-chain triglyceride concentration, which was ascribed to the better solubilization ability of mixed micelles comprising long-chain fatty acids. In case of high-fat nanoemulsions, the bioavailability is less but increases with increase in medium-chain triglyceride concentration. There are several variables that have been attributed to this phenomenon, including changes in the concentration of non-digested fat present and solubilization ability of the micelle phase. Therefore, a high β-carotene bioavailability can be accomplished either by using high-fat medium-chain triglyceride nanoemulsions or low-fat long-chain triglyceride nanoemulsions (Salvia-Trujillo et al. 2013; Zhang et al. 2016a). However, the bioavailability of carotenoids in the nanoemulsion matrix containing the mixed oil phase is dependent on the oil composition (Salvia-Trujillo et al. 2013). In another study, it has been observed that β-carotene bioavailability in oil-in-water nanoemulsion is also affected by the presence of unsaturated fatty acids (Rao et al. 2013). For instance, in comparison between corn oil, orange oil, and lemon oil, the bioavailability of carotene was higher in corn oil, which is ascribed to the presence of unsaturated fatty acids and long-chain fatty acids (C_{16} and C_{18}) which are able to generate mixed bile acid micelles that can solubilize β-carotene (Rao et al. 2013). The pH of emulsion matrix can be correlated with carotenoid chemical stability and color degradation as it propagates more during acidic condition. Xu et al. (2013) demonstrated that β-carotene is more stable at pH 6.0 and 7.0 than that at pH 3.0 and 4.0 in whey protein isolate-stabilized emulsions. A similar study was conducted in β-lactoglobulin-stabilized emulsion, where they found β-carotene degradation rate is high at acidic pH 3.0 than pH ranges 4.0–8.0 (Qian et al. 2012c).

Nanoemulsion-based encapsulation matrices have a limited scope for modulating the chemical stability of encapsulated carotenoid. This is attributed to the presence of a thin emulsifier interface layer around the oil droplet, and therefore presence of carotenoids near the interfacial layer will lead to chemical degradation stimulated by lipophobic components in the aqueous phase (transition metals, acids). In addition, carotenoids possess alternative polyunsaturated hydrocarbon chain separated by single bonds which stimulate them for autoxidation in the presence of transition metals, acidic condition, heat, light, and free radicals. Few studies are tabulated in Table 7.1, briefing nanoemulsion composition and their properties.

Nanoliposomes

Liposomes are nanometer-sized, spherical-shaped bilayer vesicles that can be created from natural cholesterol and phospholipids (Fig. 7.1). Liposomes can encapsulate both hydrophilic and lipophilic carotenoids in the aqueous core of phospholipid bilayer or at bilayer interface. However, it is not clearly known how functional molecules get released. Nevertheless, few theories suggest that liposomes digest in the liver and turn into fat, and another study suggests that body cells are hungry for phospholipid components to repair their cell structure and cell membranes; hence cells steal these materials and allow encapsulated nutrient to be released in the circulation system for absorption. Interestingly, in the case of the encapsulation of carotenoids in the liposomal matrix, the position of the carotenoids is altered in the lipid bilayer. But the location and position of the lipophilic component directly influence the dissolution capacities in the liposomes. In addition, there is a strong evidence that β-carotene can be positioned through the liposomal membrane, rather than positioned in the lipid core. Therefore, it can be concluded that the bioavailability of carotenoids in liposomes could be different compared to that of emulsified lipids or in food matrices (Tan et al. 2014c). Few studies related to liposomal encapsulation of carotenoids are tabulated in Table 7.2.

On the other hand, the bioavailability of encapsulated nutrients in any encapsulation matrix is directly correlated with nutrient dimension, matrix composition, physical integrity, and permeability of encapsulation matrix. These key factors regulate the contact area of the lipid with the enzyme and interaction between the

Table 7.1 Nanoemulsion matrix for the encapsulation of different carotenoids

Encapsulated carotenoid	Biopolymers	Matrix preparation method	Features	Reference
β-Carotene	Tween	High-pressure homogenization	Nanoemulsion droplet size was affected by emulsifier type, concentration, and homogenization parameters (temperature, cycle) β-Carotene was increasingly degraded in storage period which accounts for carotene loss about 14–25% at 25 ° C Degradation can be attributed to larger surface area and possible generation of free radicals in the course of emulsion preparation	Yuan et al. (2008a)
	Tween 20	Homogenization	Bioavailability of β-carotene was reduced in the following order of long-chain triglycerides > medium-chain triglycerides > orange oil when they were used as oil phase The bioaccessibility of encapsulated β-carotene was higher in long-chain triglyceride-based emulsions compared to medium-chain triglyceride emulsions, which is due to formation of mixed lipid micelles prompted by long-chain free fatty acids due to their larger hydrophobic cores	Qian et al. (2012b)
	β-Lactoglobulin, Tween 20	Homogenization	β-Carotene degradation was effectively retarded by addition of hydrophilic or lipophilic antioxidants Ethylenediaminetetraacetic acid comprising nanoemulsion resulted in less color loss due to ability of antioxidant to inactivate and chelate transition metals Combination of vitamin E acetate and ethylenediaminetetraacetic acid was found to be less effective at hindering color loss than individual antioxidants Protein-stabilized nanoemulsions demonstrated less color loss compared to Tween-stabilized nanoemulsions	Qian et al. (2012a)
Curcumin	OSA-modified starch	Ultrasonication	Ultrasound-assisted nanoemulsions were obtained at 7 min of sonication Curcumin loading increase had no effect on droplet size and	Abbas et al. (2014)

(continued)

Table 7.1 (continued)

Encapsulated carotenoid	Biopolymers	Matrix preparation method	Features	Reference
			charge Optimum curcumin concentration was 6 mg/mL and 0.05 volume fraction of curcumin-loaded medium-chain oil	
	β-Lactoglobulin	Homogenization	Nanoemulsions containing pure short-chain triglycerides as oil phase are not stable due to relatively high solubility of oil phase in water and Ostwald ripening effect The maximum loading efficiency of curcumin decreased with increased molecular weight The lipid digestion rate was more in the presence of long-chain triglycerides Nanoemulsions provided better physical stability than conventional emulsions	Ahmed et al. (2012)
	Tween 80, whey protein concentrate	Ultrasonication	The encapsulation efficiency was > 90% The formulated nanoemulsion was resistant to pepsin enzyme, but encapsulated curcumin was released due to the action of pancreatin enzyme Nanoemulsion was stable to pasteurization, pH stress, and salt stress; however, antioxidant activity decreased compared to free form of curcumin	Sari et al. (2015)
Lutein	Phospholipon 5G	High-pressure micro-fluidizer	Nanoemulsions demonstrated higher bioavailability than supplement Consumption of up to 6 mg of lutein as a nanoemulsion did not affect absorption of hydrocarbon carotenoids such as α- and β-carotene from the diet Lutein as a nanoemulsion may not require presence of fat for absorption as it is carried in an oil phospholipid matrix	Vishwanathan et al. (2009)

	Sodium caseinate	High-pressure micro-fluidizer	Color fading was observed during elevated temperature due to chemical degradation of lutein, and rate of color degradation was correlated with lutein degradation positively Highest droplet flocculation was observed near isoelectric point of emulsifier	Davidov-Pardo et al. (2016)
Astaxanthin	Glyceryl esters, lecithin	High-pressure homogenization	Loading efficiency of lipophilic astaxanthin was more for nanoemulsion compared to hydrogenated lecithin Co-antioxidants served in establishing strong interfacial layer and helped in better stabilization	Kim et al. (2012)
	Sodium caseinate	High-pressure homogenization	Homogenization temperature, number of passes, and pressure positively correlated with astaxanthin loss in nanoemulsion Increase in number passes both at low and high pressure resulted in astaxanthin loss	Anarjan et al. (2011)
Lycopene and astaxanthin	Tween 20	High-pressure homogenization	Emulsion droplet was higher in lycopene-encapsulated emulsions compared to astaxanthin-entrapped emulsions due to spatial orientation of pigments and interaction with oil phase	Sotomayor-Gerding et al. (2016)
Lycopene	Tween 20	High-pressure homogenization	Higher antioxidant activity was observed in nanoemulsions with a size ranging between 100 and 200 nm Nanoemulsions showed high in vitro bioaccessibility in both released and formed micelles	Ha et al. (2015)

Table 7.2 Examples of liposomal nanoencapsulation of carotenoids

Encapsulated carotenoid	Name/size of liposome	Encapsulation efficiency (%)	Features	Reference
Lutein, zeaxanthin, canthaxanthin, and β-carotene	Egg yolk phosphatidylcholine	Lutein (67.2), zeaxanthin (40), canthaxanthin (11), and β-carotene (2.5)	β-Carotene entrapment efficiency was lower compared to other carotenoids Lutein encapsulation efficiency was higher due to its different orientations, i.e., parallel and perpendicular to membrane plane	Shafaa et al. (2007)
Lutein	Egg yolk phosphatidylcholine; 83.53–134.82 nm	82.64–91.98	As the initial loading concentration of lutein increases, the encapsulation efficiency of liposome decreased Lutein entrapment location found to be at polar membrane zone	Tan et al. (2013)
Lutein, lycopene, canthaxanthin, and β-carotene	Egg yolk phosphatidylcholine	Lutein (76.4–80.2), lycopene (61.3–75.9), canthaxanthin (70.3–79.9), β-carotene (69.3–73.1)	Lutein exhibited highest antioxidant activity and canthaxanthin exhibited least antioxidant activity Entrapment of lutein and β-carotene hindered the lipid peroxidation Canthaxanthin and lycopene showed high susceptibility to lipid peroxidation As the initial loading concentration of carotenoids increases, the encapsulation efficiency of liposome decreased	Tan et al. (2014a)
Lycopene, β-carotene, lutein, canthaxanthin	Egg yolk phosphatidylcholine	–	Lutein showed higher encapsulation efficiency compared to other carotenoids Liposome physical properties were changed as a function of carotenoid concentration Lutein and canthaxanthin did not fit in liposome membrane architecture compared to lycopene and β-carotene	Xia et al. (2015a, b)

(continued)

Table 7.2 (continued)

Encapsulated carotenoid	Name/size of liposome	Encapsulation efficiency (%)	Features	Reference
β-Carotene	Hydrogenated soybean phosphatidylcholine	–	Entrapment of β-carotene-loaded liposomes in electrospun fibers conferred ultraviolet photostability of carotenoid	de Freitas Zômpero et al. (2015)
Lycopene, β-carotene, lutein, canthaxanthin	Egg yolk phosphatidylcholine	–	Encapsulation efficiency is reliant on stereochemical properties of carotenoids Lutein and β-carotene exerted mutual antioxidant activity by preventing their oxidation during preparation Controlled release was observed for lutein and β-carotene in the GI tract, while fast release was observed for canthaxanthin and lycopene	Tan et al. (2014a, b, c)
β-Carotene	Hydrogenated soy phosphatidylcholine	–	B-Carotene entrapped pro-liposomes can be formulated and stability can be enhanced in the absence of oxygen at low relative humidity	Moraes et al. (2013)
Lycopene, β-carotene, lutein, and canthaxanthin	Chitosomes (egg yolk phospholipid coated with chitosan)	Lutein (75), β-carotene (86) lycopene (87), canthaxanthin (58)	Liposome structure rigidification was observed, and it helped in controlled release of carotenoids in the simulated GI tract	Tan et al. (2016)

digestive enzyme and liposome membrane (Nik et al. 2011). In turn, entrapment of carotenoids could also control the physical characteristics of the lipid membrane and encapsulation efficiency (Gruszecki and Strzałka 2005). For instance, encapsulation efficiency of carotenoids in liposomes decreases in the descending trend: lutein, β-carotene, lycopene, and canthaxanthin. In addition, a similar trend was also observed in their antioxidant capacities. In contrast, burst release was observed for canthaxanthin and lutein in the GI tract compared to β-carotene and lycopene. The dissimilarities in carotenoid efficacy may be attributed to the different modulating effects of carotenoids (Tan et al. 2014a, b, c; Xia et al. 2015b). Thus, there might be a mutual relationship concerning carotenoid modulation in liposomal membrane and their bioaccessibility, necessitating more in-depth knowledge.

Carotenoid release rates have significant associations with the therapeutic actions of all types of encapsulation matrices. It is essential to note that carotenoid entrapped in the liposomal matrix is not accessible even after its release, and hence, the capacity of the liposomal matrix to enhance the local bioavailability of carotenoid can increase the therapeutic index. In addition, encapsulated carotenoids must be transported to the targeted site and become accessible at a level within its therapeutic index and at an adequate rate for a sustained period to have optimum therapeutic index. The action of cell-cycle-specific carotenoids such as lycopene and β-carotene can be highly sensitive to the release rate; hence with the help of the liposome, it is possible to tune the rate of release as per the required therapeutic application (Gloria et al. 2014).

The biological importance of dietary carotenoids evidently differs by their chemical and physical properties. Liposomes have a problem with their delivery mechanism such as how to transport functional molecule across cell membranes to intracellular sites of action. Lipophilic carotenoids can enter cells as free carotenoids in a weak base environment by passive diffusion and decrease concentration gradient in the uncharged form, while small lipophobic carotenoids can use cell membrane transporters to enter into intracellular sites of action (Chithrani et al. 2010; Peng et al. 2010). Hence, passive delivery of nutrients via the circulation of the encapsulated liposome molecule to the targeted site with release of the nutrient in accessible form near or at its anticipated site of action at a concentration that exceeds the minimum therapeutic concentration results in better functionality. However, liposome multitude characteristics help in the rational design to accomplish required therapeutic objectives.

Nanoclusters of Emulsions

Clustered nanoemulsions are formulated by controlled flocculation or aggregation of lipid droplets (Fig. 7.1). Flocculation can be hetero- (unlike fat droplets) or homo-flocculation (similar fat droplets) (McClements 2012). A nanoemulsion containing flocculated droplets has different physicochemical properties such as optical transparency, stability, appearance, rheology, and adsorption in the gastrointestinal tract. During formulation of functional foods, the final texture decides the possible bioactive compounds that can be incorporated into the matrix. In this way, viscosity and ingredients in the functional food matrix influence the structural design principles (McClements and Li 2010). For example, flocculated nanoemulsion possesses high viscosity compared to non-flocculated nanoemulsions at the same oil droplet concentration due to large effective volume fraction. Depending on the oil droplet concentration, flocculation leads to formation of paste-like or gel-like structures. Clustered emulsions can be used to deliver two bioactive compounds at once. However, properties of clustered emulsions can be useful in masking undesirable flavor or feature of other bioactive compounds. However, utilization of nanoclusters for the encapsulation of carotenoids is still under development, and in the future co-encapsulation of carotenoids with other functional molecules is possible with these nanostructures.

Nanomicelles

Nanomicelles are self-assembled functional molecule carriers. Casein micelles are considered as the prototype in designing nanomicelle structures to deliver therapeutic nutrients and their possible applications. Model micelle-based encapsulation matrix is depicted in Fig. 7.1.Various factors such as presence of disulfide bonds, hydrogen bonds, electrostatic and hydrophobic interactions, Ca^{2+}, salt concentration, temperature, van der Waals forces, temperature, and ionic strength define the stability of a micelle during encapsulation of carotenoids. Biopolymer-based nanomicelles are currently growing in pharmaceuticals and food industry as encapsulation matrices due to their higher blood circulation time. It has been observed that micellar form enhances the cellular uptake of encapsulated nutrients (Trivedi and Kompella 2010). The advantages of nanomicelles include direct incorporation of encapsulated functional ingredients into final products, intestinal release of micellated nutrient, and enhanced bioavailability of functional compounds.

In a study performed by Sáiz-Abajo et al. (2013), they demonstrated the suitability of casein micelles to encapsulate labile β-carotene by shielding them against degradation during the common industrial stabilization process such as pasteurization, sterilization, heating, baking, and high hydrostatic pressure. The casein nanomicelles provide thermal protection during the industrial processing of ingredients, additives, and food products. However, during digestion, casein will get denatured followed by release of entrapped nanoencapsulated nutrient into the bloodstream for cellular uptake.

7.2.2 Solid Matrices

Nanocrystals and Nanoparticles

Nanocrystals enclose a crystallized bioactive agent surrounded by polymers or surfactant-assisted stabilizer. They have been developed to achieve adequate bioavailability of hydrophobic functional compounds in aqueous media. Unlike lipids and polymer nanoparticles where a bioactive is encapsulated, the organic composition of the compound itself assists as a solid matrix of nanoparticles, thereby eliminating the problem of compatibility with the matrix. Nevertheless, a crystal-based nanoencapsulation matrix is most effective for functional compounds having high melting temperature, that is, the ability of a functional compound to crystallize at room temperature (Brough and Williams 2013). Nanocrystals provide the most advanced benefits to the food industry, such as improved formulation performance, dissolution rate, and increased saturation solubility of bioactive compounds. In addition, their high loading capacity allows efficient transport of bioactive compounds to or into cells, which have a sufficient concentration for the desired functional effect.

On the other hand, nanocrystals are particles comprising only encapsulated nutrients without any matrix materials such as polymers (in polymeric nanoparticles) or phospholipids (in liposomes). Nevertheless, nanocrystals are stabilized only by a sterically stabilized polymer layer or adsorbed surfactant layer. These stabilizing layers on nanocrystals range between 2 and 10 nm in thickness. From the point of view of the cubic system, nanocrystals of 500 nm in size and the adsorption layer as part of the nanocrystals account for up to 6% of the total volume. In practice, nanocrystals can be regarded as nanoencapsulation matrices with 100% loading efficiency (Kinder et al. 2011; Lin et al. 2012). Nanocrystals transport a functional molecule to the target sites and help in permeation of active compound in molecular form through cellular membranes and barriers. Nanocrystals can be fabricated by bottom-up and top-down techniques. The conventional precipitation process involves adding a non-solvent to the compound solution to obtain crystalline nanoparticles. The top-down approach is best suited for industrial production of homogeneous nanocrystals using high-pressure and bead mill technologies (Lin et al. 2012).

Nanoparticles enhance the therapeutic index of entrapped functional molecules through altering pharmacokinetics, protecting from enzymatic action, providing sustained release, and reducing toxicity. Recently, carotene nanoparticles were fabricated for food industry such as Lucantin or Leucarotin by BASF. Lucantin is a source of xanthophylls, and Leucarotin is a source of β-carotene used as feed additive and food additive, respectively (Mirza 2017). For preparation of these nanoparticulate carotenoids, oil-in-water emulsion was the base where carotenoids were solubilized in oil phase. Thus, the prepared emulsion was lyophilized, and it was reported that 90% of encapsulated carotenoid was in amorphous state. These amorphous crystals are called nanomorphs and they are marketed under the trade name Nanomorph. These were found to have higher saturation solubility when compared to crystalline material. Recently, Arunkumar et al. (2013) studied the structural interaction between lutein and low molecular weight chitosan to produce lutein-encapsulated nano-chitosan. It was observed that encapsulated lutein can be re-extracted in its native state due to weak bondage between lutein and cross-linked chains of low molecular weight chitosan in the presence of water molecules. Further, it was observed from in vitro and in vivo studies that lutein absorption was higher in nanoencapsulated chitosan indicating nanoencapsulated lutein can be considered as a better dietary supplement in functional food formulations.

Coacervates

Coacervates are insoluble complexes formed between two or more biopolymers by means of electrostatic interactions (Fig. 7.2). The concentration and composition of the biopolymer and environmental conditions such as the ionic strength and pH are directly related to the loading efficiency of capsules produced using coacervates. The commonly used biopolymer compositions include alginate-polylysine, gelatin-gum arabic, albumin-gum arabic, and gelatin-carboxymethylcellulose. Coacervates are formulated by dispersing the base biopolymer in solvent followed by suspending the therapeutic material. Base biopolymers interact electrostatically to form coagulates and entrap the therapeutic materials to stimulus such as change in pH, inorganic salts, electrolytes, and temperature. Capsules formulated using coacervation technique are heat-resistant and provide sustained-release profile under various temperature and mechanical stresses. Silva et al. (2012) encapsulated lycopene by complex coacervation using gelatin and pectin as the encapsulants, but the process did not improve the stability of the pigment due to loss of initial coacervate structure and disintegration during freezing. Hence, postprocessing operations play a crucial role in the functionality of encapsulated carotenoids. A study conducted by Rocha-Selmi et al. (2013a) shows that the capsules obtained by complex coacervation have a better capacity to impart color to the food matrix. This might be attributed to the homogenous distribution of the pigment and the structural compatibility with the food matrix. However, presence of a homogenous distribution of the pigments in the encapsulation matrix prepared by complex coacervation demonstrated the less cake pigmentation. This might be an outcome of matrix incompatibility and elevated processing parameters. During the preparation of the mix, the microcapsules were not dissolved, and the heat of the oven was not sufficient to break them up completely, and thus the core was not fully released and distributed throughout the cake, which restricts the direct use of freeze-dried coacervated microcapsules in this type of application (Rocha-Selmi et al. 2013b). Qv et al. (2011) observed that encapsulation of lutein in gelatin and gum arabic enhances the deteriorative effect against light, temperature, and humidity. In addition, the retention rates of lutein entrapped in capsules were 92.86% at 4 °C, 90.16% at 25 °C, 90.16% with relative humidity of 33%, and 90.25% under aerobic condition.

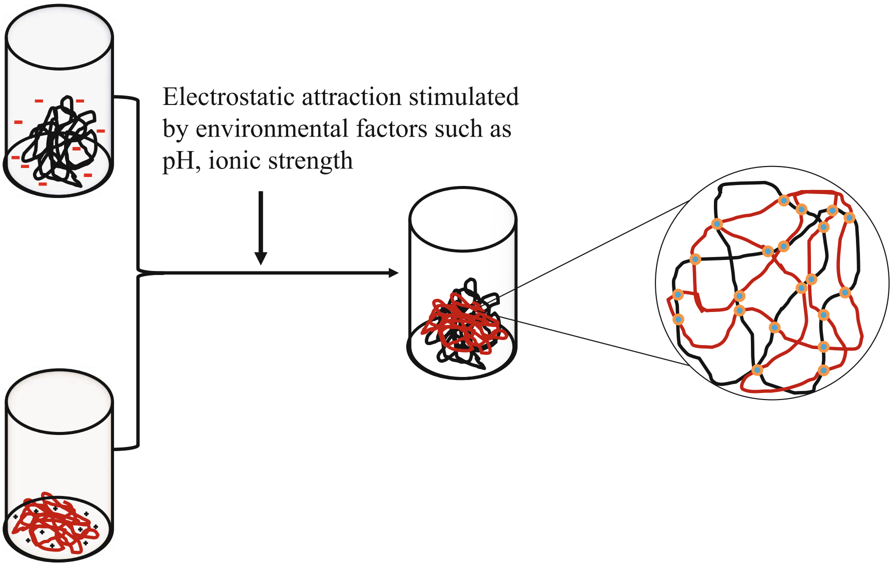


Fig. 7.2 A schematic illustration of heterogeneous homogeneity of coacervate encapsulation matrix

7.2.3 *Semisolid Matrices*

Hydrogel Beads

Hydrogels are effective in protecting nutraceuticals from external stresses. As the gel structures can be modulated by changing the concentrations of oil fractions, gelling agents, magnitude of triggering forces, and duration of gelation, it is possible to produce gels with desired properties such as permeability and hardness, making the gels to have different sensitivities to environmental stresses (temperature, pH, enzyme, mechanical forces). Therefore, hydrogels can be used to modulate the release of functional compounds. A model hydrogel matrix is illustrated in Fig. 7.3. Mun et al. (2015a) designed rice starch gels containing protein-stabilized fat droplets (filled hydrogel), which were used to deliver β-carotene in simulated digestive conditions. The study indicated that β-carotene in the gels had higher bioaccessibility than that in ungelled emulsions or hydrogels without fat droplets, and this finding was attributed to the higher aggregation stability of the fat droplets in the gelled network. A following study by the same group reported that emulsifier type (WPI or Tween 20) or starch type (rice starch or bean starch) did not influence the bioaccessibility of β-carotene in the gel matrix (Mun et al. 2015b).

Zhang et al. (2016b) fabricated alginate-based hydrogel beads in which an encapsulating matrix partly protected the β-carotene from autoxidation and other chemical degradations. This property of encapsulation matrix was demonstrated as a function of polymer concentration in the beads. However, in simulated digestion

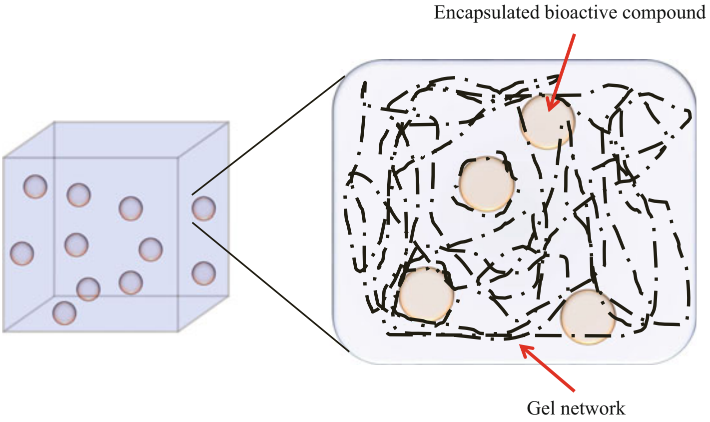


Fig. 7.3 A schematic illustration of hydrogel bead encapsulation matrix

studies, alginate hydrogel beads retarded the rate of digestion and the extent of lipid digestion which is attributed to smaller pore size and higher bed diameter. The bioavailability of β-carotene was higher when it was entrapped within free oil droplets than within hydrogel beads. This result demonstrates that β-carotene remained entrapped within undigested lipid droplets, and only fewer micellated carotenes were generated to solubilize the released β-carotene molecules. Therefore, this type of hydrogel bead matrices may be suitable for hindering the chemical degradation of carotenoids during food processing and storage or within the GI tract, nevertheless with the compromise of bioavailability of carotenoids.

7.3 Nanopatterning of Different Encapsulation Matrices

7.3.1 Patterning Based on Size Reduction

Size reduction-based patterning technique is attractive because it occurs spontaneously, in a natural manner, without any intervention. However, suitable encapsulation matrices must be formulated for better efficiency. For instance, when pressure force is utilized, pressure pattern must be located in intimate contact with the matrix for the formation of nanostructures. In case of sonication force, this involves imploding cavitation force in crude encapsulation matrix such as emulsion, resulting in formation of nanoencapsulation matrix. Spray drying is a cost-effective solid-drying process achieved by atomizing emulsion containing encapsulating polymer and encapsulants (high surface to mass ratio) with a high-temperature gas causing dewatering uniformly. Utilization of these techniques for encapsulation of carotenoids is discussed below along with their process parameter consideration.

High-Pressure Homogenization

High-pressure homogenization technique is normally utilized in patterning of nanoemulsions. In this process, fluid is passed through a valve as a consequence of high turbulence, shear stress, and cavitation microstructure disruption, creating uniform-sized nanostructure leading to enhanced physical stability and better textural characteristics (Fig. 7.4a). However, when high pressure is used for production of tomato puree and concentrates, pressure may hinder the bioaccessibility of carotenoids. This is attributed to the fact that a fiber network formed during pressure-assisted homogenization limits the carotenoid micellarization (Colle et al. 2010; Panozzo et al. 2013; Svelander et al. 2011); this is also supported by the increase in pulp viscosity after homogenization (Bayod et al. 2007; Bayod and Tornberg 2011). However, homogenization changes the cell structure by separating the fibers and permitting their end group to bind higher amount of liquids causing thicker consistency (Palmero et al. 2016). These observations suggest that natural structural barriers and presence of insoluble/soluble phases influence the in vitro bioaccessibility of carotenoid upon high-pressure homogenization. In general, carotenoid bioaccessibility can also be correlated with homogenization pressure. For instance, high in vitro bioaccessibility of lycopene can be expected with small droplets prepared using high-pressure homogenization (Ha et al. 2015). However, presence of long-chain fatty acids enhances the solubilization of astaxanthin through formation of micelles (Sotomayor-Gerding et al. 2016).

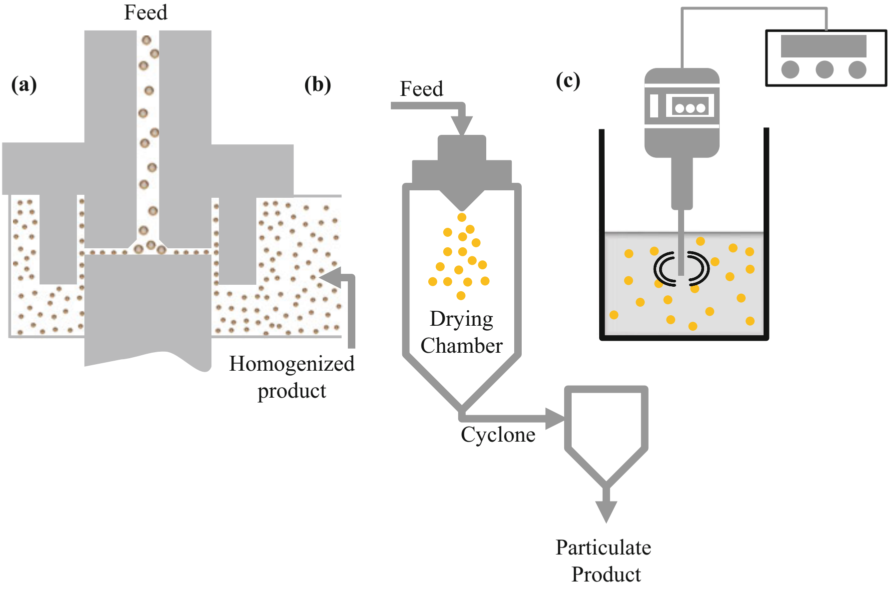


Fig. 7.4 Schematic illustration of different nanostructure fabrication processes: (**a**) High-pressure homogenization, (**b**) spray drying, and (**c**) sonication

Ultrasonication

Ultrasonication is used as a homogenization technique in food industry; however, cavitation technique is also used in patterning of emulsions. Ultrasonic waves are generated by sonotrodes or acoustic horns using applied electrical energy. Ultrasonic wave frequency generally ranges from 20 to 40 kHz and produces high shear force and mechanical effects (Fig. 7.4c). Different applications and purpose of ultrasound used in food processing include uniform heat transfer in freezing or crystallization, improved drying, increasing mass transfer in marinating or pickling, degassing of liquid foods, enhanced filtration, and vibrations in demolding, defoaming, oxidation, and homogenization. In addition, ultrasonication is also used in the preparation of oil-in-water emulsions. The purpose of using ultrasound in emulsification is to reduce the size of droplet uniformly within a narrow size distribution using acoustic cavitation phenomenon. The effectiveness of ultrasound-assisted emulsion depends on several process variables such as biopolymer concentration, sonication time, and sonication power (Abbas et al. 2014).

Ultrasound-assisted patterning of emulsions causes overprocessing problem at higher-energy density, resulting in increase in droplet size. In other words, the intensity of ultrasonication is a function of operation time and power, while the intensity increases the rate of droplet breakage in the dispersion medium. Nevertheless, a similar effect can be observed at less emulsifier concentration and if the emulsifier is not able to adsorb quickly at the new droplet interface. Emulsifiers promote the creation of interfacial film for reducing the surface tension. Hence, emulsifier properties help in tailoring of emulsion encapsulation matrix with lower droplet size assisted by ultrasound. However, there is lack of research studies concerning sonication parameters' influence on bioavailability and bioaccessibility of carotenoids. This might be due to scale-up limitation of the technology in encapsulation sector. In addition, ultrasonication is used only in fabrication of nanostructures, where nanostructure property can be correlated with carotenoid functionality and bioavailability in the GI tract (Abbas et al. 2014; Sari et al. 2015).

Spray Drying

Spray drying consists of four main stages, which include atomization, spray contact with drying medium, evaporation, and separation of product from airflow (Fig. 7.4b). Spray drying is commonly achieved by dissolving, dispersing, or emulsifying the sensitive ingredients in an aqueous solution of coating material, followed by atomization and spraying of the mixture into a drying chamber. The droplet and drying medium (typically hot air) is contacted and the solvent is evaporated; then the dried particles are separated in a cyclone from the humid air and collected in powder form. Efficiency of encapsulation of bioactive substances by spray drying is affected by a number of factors, including outlet and inlet air temperatures, type of wall material, and drying time. Primarily, wall material should provide protection for the core material. This choice should be mainly based on the physicochemical properties of a carrier material, such as solubility, molecular weight, good film-forming properties, glass and melting transitions, diffusibility, crystallinity, and emulsifying properties. This material should be also cheap, food grade, bland in taste, and biodegradable. The disadvantage of this process is limitation of carrier material and concentration of pigment. After encapsulation by the spray drying process, particles with a spherical shape, usually with a lot of wrinkles and dents, are obtained, but it also depends on the drying conditions and carrier material. Wrinkles are usually formed on the surface of the particles due to shrinkage during the spray drying process (Mahdavi et al. 2014). This is attributed to the fact that at low inlet air temperatures, less water evaporated and the particles had more time to shrink, while at higher inlet temperature, rapid evaporation could lead to particle shrinkage (Rajabi et al. 2015). Particles of carotenoids have uniform particle size, low bulk density, moisture content below 5–8%, and good thermal stability (Kandansamy and Somasundaram 2012).

Spray drying of carotenoids is the most popular method for carotenoid protection. Moreover, its simplicity and flexibility (different carrier agents, changes in drying parameters) allow us to increase protection, yield, and encapsulation efficiency. The most common wall materials used in preparation of spray-dried powders include maltodextrin, gum arabic, and modified starch. Maltodextrin is a polysaccharide that is used as a food additive; its properties vary depending on the extent of starch hydrolysis. The disadvantages of these substances can include a lack of emulsifying ability and the possibility of active components' limited retention (Kandansamy and Somasundaram 2012; Kha et al. 2010). The main advantage of gum arabic is its low viscosity in aqueous solutions, which facilitates the encapsulation of many substances. Gum arabic forms very stable emulsions. When combined with maltodextrin, it results in better retention of encapsulated substances and better protection against oxidation (Kandansamy and Somasundaram 2012; Özkan and Bilek 2014). Moreover, gum arabic provides more resistance to structural deformation due to the high permeability as the wall material. Modified starches possess low viscosity and bale to use at a high concentration relative to the total emulsion. This high concentration of the shell level in the emulsion reduces the possibility of loss of carotenoids in the encapsulation by spray drying (Özkan and Bilek 2014). In addition, use of combined carrier polymers can enhance the encapsulation efficiency. For instance, combining whey protein and gum arabic enhanced the encapsulation of astaxanthin oleoresin up to 70% in comparison with gum arabic mixed with maltodextrin (Bustos-Garza et al. 2013). Spray drying as a microencapsulation method for carotenoids is a good method for its protection. However, it has numerous limitations, and there is no single set of optimal conditions for each carotenoid sample. It is necessary to test each time the type and amount of carrier addition, inlet and outlet temperature, feed flux, type of atomizer, and speed of spray disc, and what is more, when a scale-up is needed, usually new tests are needed. Nevertheless, it allows one to obtain a product with varying physical properties, through the use of drying parameters, such as temperature, feed flux of raw material stream, and the concentration of carrier solution. Moreover, the process is cheap and a good-quality product is obtained.

Alternatively, electrospraying is emerging as a promising technology for encapsulation of carotenoids as it allows processing at room temperature. In electrospraying an electric field is used to reduce the particle diameter. When an electric field is applied to a particle, a force called Coulomb force is generated inside the particle, which competes with cohesion force; when it dominates over cohesive force, a diminution in surface tension results in formation of nanoparticle (Pérez-Masiá et al. 2015). Recently, emulsion-electrospraying technique was used to encapsulate lycopene and compared performance of the obtained structures with those obtained by spray drying. Their results showed that much higher encapsulation efficiencies were obtained through electrospraying, due to the thermal degradation of lycopene upon spray drying (Pérez-Masiá et al. 2015). β-Carotene has been studied under electrospraying techniques and encapsulated within zein and whey protein concentrate structures. Though the encapsulation efficiency was higher, emulsion stabilizing polymers play a crucial role in efficiency and protection against thermal degradation (Gómez-Mascaraque et al. 2017).

7.3.2 Patterning Based on Surface Functionalization

Nanopatterning entangles a wide range of surface modification strategies that are essential in tailoring of nanoencapsulation matrices. The basic concept of patterning based on surface functionalization is to make the nanoencapsulant surface active at the intended places such as interface and shell surface. This section will emphasize mainly surface modification techniques through interaction between bulk polymers and encapsulating materials at monolayer level occurring at the interface.

Precipitation Techniques

In precipitation-based patterning approach, the active compound and polymer are co-precipitated, generating fine nanoparticles of the functional compound impregnated into polymeric matrices. In this technique release of active compound into food matrix during storage or into the GI tract can occur by diffusion or degradation, depending on the type of polymer used. Diffusion process takes place when the solute passes through the polymer chain or pores. On the other hand, polymers may degrade within the food matrix as a result of hydrolysis, resulting in release of encapsulated active compound. However, in this case, polymer molecular mass and chemical structure governs the degradation process. The supercritical CO_2 acts as an anti-solvent to reduce the solubility of the solutes in the mixture and causes supersaturated precipitation of solutes in the form of nano- or microparticles. The phase behavior of the involved system plays a crucial role in understanding the precipitation mechanism, such as jet breakup, nucleation and growth kinetics, and mass transfer, as well as in determining the most satisfactory operating conditions during precipitation. It was observed that lecithin had provided better stability to precipitate lycopene (Cheng et al. 2017). In addition, the precipitation pressure presented a positive effect on the mean particle size of β-carotene, whereas the anti-solvent flow rate showed a negative effect on this variable (Franceschi et al. 2008).

Molecular Interaction

Molecular interaction-based patterning techniques include inclusion complex formation, gelation, self-assemble, and cross-linking.

Inclusion Complex Formation The formation of inclusion complexes is limited by the size, shape, and hydrophobicity of the guest molecules. It is not feasible to include some bioactive compounds of interest in amylose complexes based on current knowledge and techniques. For example, carotenoids such as β-carotene and lycopene are highly conjugated long-chain isoprenoid micronutrients and have very low solubility in a number of common solvents, e.g., water, dimethyl sulfoxide, and ethanol. Their extremely low solubility limits their bioavailability and prohibits the direct formation of amylose guest inclusion complexes, since a finite water or DMSO solubility is generally required to transport the guest into the hydrophobic core of the amylose helix (Kong et al. 2018). However, the effective encapsulation depended on the emulsifying effect of the surfactants to dissolve β-carotene and bring β-carotene molecules to the amylose crystalline phase (Kong et al. 2018; Kong and Ziegler 2014).

Cyclodextrin molecules have demonstrated better host-guest molecule interaction by formation of inclusion complex. Hydrophobic molecules can be complexed with cyclodextrin to enhance the solubility in water-rich matrices (Celik et al. 2017; Fernández-García and Pérez-Gálvez 2017; Lobo et al. 2017). The resultant non-covalent host-guest or inclusion complexes are of present technological and scientific interest for their unique chemical, biological, and physical tunable characteristics. Such non-covalent associations can enhance the bioavailability, hydrophilicity, and stability of guest molecule, thereby modulating the sustained-release mechanism (Lobo et al. 2017; Yuan et al. 2012). Chen et al. (2007) have described preparation of astaxanthin with β-cyclodextrin; the formulated inclusion complex exhibited better water solubility (<0.5 mg/mL) than that of un-complexed astaxanthin itself. In addition, inclusion complex demonstrated more stability to light and heat. In another study, by Yuan et al. (2008b), inclusion complex of astaxanthin with hydroxypropyl-β-cyclodextrin using IR spectroscopy enhanced the water solubility of complex >1.0 mg/mL, which is higher than (Chen et al. 2007) formulated inclusion complex. On the other hand, it was observed that the assimilation efficiency of β-cyclodextrin inclusion complex of carotenoids increased in comparison with carotenoid suspension in Tween. This particular observation between the β-cyclodextrin complexed and the corresponding Tween suspension is that, a priori, the maximum concentration of the guest compound is limited by its solubility in suspension (Fernández-García et al. 2010).

Gelation This nanopatterning technique utilizes the ability of polymers to generate a gel network by thermal or ionic gelation. Pectin and alginate gelation induced ionically by calcium ions is an example for ionic gelation (Soukoulis and Bohn 2018). A typical gelation-based patterning involves formulation of a biopolymer solution and dissolving or dispersing them in the solution of functional molecules to be encapsulated. Thus, the formed solution is dispersed in edible oil, thereby producing water-in-oil emulsion in the presence of food-grade surfactant. Resultant emulsion droplets are gelled with the assistance of salts (in case of ionic gelation) or heat (in case of heat-induced gelation, matrix is cooled below gel temperature of polymer that forms the encapsulation shell). After gelation process, gelled emulsion droplets will be separated from oil followed by drying the gelled capsules to form a free-flow powder.

In case of pectin-alginate gel network formation, an intermolecular interaction zone between carboxyl groups of galacturonic acid or guluronate residue and divalent cation provides the template for encapsulation of different functional ingredients. However, salt-induced cross-linked pectin-alginate hydrogels exhibit a heterogeneous structure due to clusters of ionically allied domains in the gel matrix (Hoffman 2012). Therefore, reinforcement of pectin-alginate beds with other polymer mixtures is essential. In addition, it is possible to encapsulate both hydrophilic and lipophilic bioactive compounds using hydrogels formulated by ionic gelation of emulsion (Belščak-Cvitanović et al. 2016). However, encapsulation efficiency of gel matrix in hydrogels is not reliant on the particle size, but gelling material/biopolymer combination decides the fate of functional molecule loading efficiency and protection in the GI tract. For instance, whey protein demonstrated the matrix compatibility and enhanced the encapsulation efficiency of β-carotene in combination with alginate. In addition, whey proteins impede the filler effect and preserved the morphological characteristics of dried beads (Belščak-Cvitanović et al. 2016). In a priori knowledge, the egg-box structure of sodium alginate induced by interacting with Ca^{2+} found wide technological applications in food packaging, coating, texturing, restructuring, and encapsulation of enzymes, functional compounds, and living cells (Banerjee and Bhattacharya 2012; Comaposada et al. 2015; De Prisco and Mauriello 2016; Li and Nie 2016). Encapsulation of carotenoids in Ca^{2+}-induced sodium alginate gel matrix using emulsions as template ensures the chemical stability and better bioavailability compared to that of carotene-rich fruits and vegetables (Soukoulis et al. 2016).

Self-Assembly Biopolymers can assemble spontaneously onto other surfaces using specific chemical interactions. In general, biopolymers contain a functional group which has an affinity toward the surface to be improved. However, surface functionalization is driven by the specific surface-molecule interaction boundaries. In addition, the nature of bond formed between the modifier and surface helps in mobility of molecules on the surface after adsorption by forming a structured monolayer. Self-assembled molecules are stabilized by the intermolecular interactions between the surface and molecules. These interactions along with surface mobility permit functional molecules in low-coverage areas to migrate to a more ordered domain, resulting in formation of a homogenous encapsulation matrix. Recently, micellar nanostructures formulated via self-assembly of biopolymers have exhibited great potential as a nanodelivery vehicle for biomedical application (Rösler et al. 2012).

In a recent study, nanomicelles were formulated via conjugation between linoleic acid and hydroxyethyl cellulose through self-assembly to entrap β-carotene, which is driven by the gain in entropy of solvent molecules (Guo et al. 2012; Yang et al. 2016). The fabricated nanomicelles exhibited the sustainable release and good encapsulation efficiency (Yang et al. 2016). Jarunglumlert et al. (2015) studied the encapsulation characteristics of aggregated casein and reassembled micelles entrapped with β-carotene via lipophilic interactions. Aggregated and reassembled caseins were fabricated by modulating the pH and addition of salt to sodium caseinate solution, respectively. The result demonstrated the pH influence on encapsulation efficiency. However, both the nanostructures enhanced the storage stability of β-carotene. On the other hand, reassembled casein micelles can also protect the entrapped β-carotene from degradation process during baking, heating, and high-pressure processing (Sáiz-Abajo et al. 2013).

Cross-Linking Cross-linking technique is used in the formulation of a polysaccharide-protein complex. In this strategy, the droplets present in the encapsulated matrix are hardened by covalent cross-linking and are directly transformed to the analogous capsules. The cross-linking process can be induced either using a cross-linking agent or heat. Fabrication of cross-linked hydrogels has attracted researchers due to their better degradation rate, mechanical strength, and swelling properties. However, suspension cross-linking is an adaptable technique and can be implemented for the entrapment of insoluble, soluble, solid, and liquid materials and for the formulation of nanocapsules (Altunbas et al. 2011; Moffat and Marra 2004). Genipin is a nontoxic natural cross-linking agent. Encapsulating bead prepared by cross-linking κ-carrageenan and sodium carboxymethylcellulose using genipin helped in the sustained release of β-carotene. This sustained-release mechanism is beneficial for extending the residence time of functional molecules. However, the release of β-carotene from beads reduced with the increase in genipin concentration. Hence, it can be concluded that the release rate of β-carotene from a cross-linked bead is the function of swelling ability of the matrix (Muhamad et al. 2011).

Electrostatic Deposition

Modifying an encapsulation surface with nanocoating of biopolymers can change the characteristics of the interface. The nanolayer can impart physical or chemical feature which is essential for the surface to protect the functional compound present in the matrix (Tan et al. 2016). Electrostatic deposition is a non-covalent coating; biomaterials are generally adsorbed on the surface of particles via weak molecular interactions such as electrostatic interaction, hydrogen bonds, and hydrophobic interactions. For instance, protein-based nanostructures possess amino acids and carboxyl groups that provide surface charges, whereas hydrophobic groups sit in the core of protein-based nanostructures. Therefore, electrostatic interaction can be applied between protein nanostructures by coating their surface with oppositely charged biopolymers. On the other hand, emulsifier with a hydrophobic site at one end and a hydrophilic site at the other end can non-covalently adsorb with hydrophobic groups of protein-based nanoparticles via hydrogen bonds and hydrophobic interactions (Lohith Kumar and Sarkar 2017). As a result, the hydrophilic groups can be exposed on the surface of protein-based nanoparticles. These non-covalent coatings can alter the physical and chemical properties of protein-based nanoparticles, which would stabilize nanoparticles in the gastrointestinal tract and improve their uptake efficacy for better absorption of encapsulated phenolic phytochemicals.

7.4 Designing Food Matrices for Nanoencapsulated Carotenoids: Role of Excipients in Protection of Carotenoids in the GI Tract

Designing food matrices specifically to enhance the efficacy of nutraceuticals may be facilitated using excipients. Excipient foods, beverages, and ingredients are intended to be co-consumed with foods rich in nutrients and nonessential, but health-promoting, compounds that are poorly absorbed (Liu et al. 2016; Salvia-Trujillo and McClements 2016a, b). Examples of such excipient foods proposed include dressings, sauces, yogurt, ice cream, spreads, confectionaries, and beverages. The increased bioavailability of carotenoids in a raw vegetable and fruit salad when co-consumed with various oils, i.e., an excipient ingredient, supports the concept that select excipients promote absorption. Incorporation of natural and synthetic emulsifiers in foods represents another strategy for increasing the bioavailability of dietary lipophilic microconstituents (Marze 2015).

Excipient foods and ingredients can increase the absorption of dietary carotenoids and other lipophiles by facilitating one or more processes associated with the bioaccessibility and bioavailability of fat-soluble microconstituents in the diet. These include enhanced liberation from the food matrix, solubilization within lipid droplets, digestion of bulk lipid to facilitate the formation of mixed micelles, increased transit time within the gut, uptake from micelles by absorptive epithelial cells, and stimulation of the assembly and secretion of chylomicrons into lymph. Studies in model systems have shown that the impact of excipients on the bioaccessibility of carotenoids is subject to modulation by various factors. For example, the size of the oil droplets and types of oil (e.g., vegetable oil rich in long-chain vs. medium-chain FA) have been reported to affect carotenoid bioaccessibility during digestion of oil-in-water emulsifications (Liu et al. 2015; Salvia-Trujillo and McClements 2016a, b; Zhang et al. 2016c).

The efficacy of functional compounds present in dietary supplements, foods, or drugs is principally being governed by their absorption kinetics in the GI tract. In the transformation of the nutrient and bioactive molecules, its liberation during digestion and absorption into cells strongly depends on the grafting carrier matrix. Thus, the choice of a matrix and its interaction with bioactive molecule or nutrient is a key issue. Additionally, this matrix may also serve added benefits preventing the loss of the part or adverse interactions with inhibitors of absorption. In general, in many health-promoting molecules, bioavailability is low in humans, which is attributed to their poor absorption profile, susceptibility to degradation, and low bioaccessibility. However, the pathways that govern the bioavailability of bioactive molecules are multifaceted, which include liberation from ingested supplement, solubilization in gastrointestinal fluids, and transport into or out of epithelial cells and/or chemical transformations.

In addition, the components of food matrix might inhibit or favor the said pathways of bioactive compounds during digestion. There are several approaches such as utilization of colloidal systems that can be used to enhance this liberation and solubilization of bioactive compounds. In this approach, a functional molecule is solubilized in the oil phase and can be incorporated in the food matrix. On the other hand, bioactive compounds might be left in their natural source such as vegetable or fruits and co-ingested with specific formulation able to boost their efficacy. In this context, excipient matrices can be used in enhancement of bioavailability of carotenoids; however, excipients might or might not have an inherent bioactivity themselves, but when they are co-ingested with other foods, they can boost the bioactivity of any bioactive compound present.

There are examples that support the use of foods as excipients to increase the absorption of carotenoids from plant foods rich in these pigments. As previously mentioned, Kopec and colleagues found that co-consumption of fresh avocado, a high-fat fruit, with a breakfast meal that included either high β-carotene tomato sauce or raw baby carrots markedly increased provitamin A absorption and the production and absorption of retinyl esters (Kopec et al. 2014). Similarly, addition of three scrambled eggs to a carotenoid-rich, raw mixed-vegetable salad containing 3 g canola oil also significantly increased the absorption of α- and β-carotenes, lycopene, lutein, zeaxanthin, and α- and γ-tocopherols (Kim et al. 2015, 2016). Further investigation of foods and beverages that may increase the absorption of carotenoids from fruits and vegetables, such as whole milk (Xavier et al. 2014), yogurt, and ice cream (Soukoulis and Bohn 2018), merits consideration.

Selected foods and ingredients may also diminish carotenoid solubility and uptake. Preclinical studies suggest that citrus fruit flavanones may affect the bioaccessibility and absorption of carotenoids. Boiled and pureed orange-fleshed sweet potato (OFSP) was digested in vitro alone or with either pink or white grapefruit juice. Addition of pink grapefruit juice decreased micellarization of both all trans- and 13-cis-β-carotene in OFSP by approximately 35%, and micellarization of these carotenoids was further suppressed in samples containing white grapefruit juice (Poulaert et al. 2012). Additional experiments supported the likelihood that naringin, the most abundant flavanone in grapefruit, was the predominant antagonist of the transfer of β-carotene into micelles. Intestinal cell uptake of β-carotene from micelles generated during digestion of OFSP only and OFSP mixed with pink grapefruit juice was similar. In contrast, uptake of both β-carotene and β-cryptoxanthin from physiologically relevant mixed micelles by Caco-2 cells was increased in the presence of 50-fold excess of hesperitin-aglycone, hesperitin-glycone, and naringin (Claudie et al. 2013). Hesperidin also increased intestinal activity of BCO1 in Mongolian gerbils fed a diet without β-carotene (Poulaert et al. 2012). These preliminary findings support the need for additional research evaluating the potential use of citrus fruits and beverages, as well as foods rich in other classes of polyphenols, as excipients for enhancing the absorption and metabolism of carotenoids.

Several groups have addressed the possible impact of minerals (calcium, magnesium, iron, zinc, and sodium) on the in vitro bioaccessibility of carotenoids (Eric Biehler et al. 2011; Corte-Real Biehler et al. 2016). Mineral concentrations were chosen to mimic levels achieved after consuming a meal containing minerals as well as levels achieved after supplement intake. A concentration-dependent reduction in micellarization of tested carotenoids was observed with calcium, iron, and zinc in both studies. More recently, it was demonstrated that the addition of 500 mg calcium carbonate to a complete meal containing tomato paste delivering 19 mg all trans-lycopene decreased its bioavailability by 83% in healthy individuals (Borel et al. 2016). Parallel in vitro experiments revealed that micelle size and the extent of incorporation of lycopene were not affected by calcium, but that the zeta potential (electrical charge) of the mixed micelle was decreased by the divalent cation. It was suggested that this reduction in zeta potential may adversely affect interaction of the micelle with SR-B1 on the apical surface of the absorptive epithelium. Magnesium, at high physiological concentrations, negatively affected the bioaccessibility of carotenoids from a spinach matrix in vitro, at two different concentrations of bile (1 or 8 mM) and pancreatin (100 and 900 mg/L) (Corte-Real et al. 2018). This suggests an inhibitory effect of magnesium on carotenoid bioaccessibility over a range of different digestive conditions, possibly more reflective of an in vivo adaptive situation. However, the effect of magnesium was especially accentuated in the presence of low bile concentrations (1 mM) and, to a lesser extent, at low concentrations of pancreatin (100 mg/L), indicating that under such critical concentrations, the negative effect of magnesium, and other divalent cations, is more pronounced. Although bile concentrations as low as 1 mM are not normally found in vivo in healthy subjects, we could imagine this happening in, e.g., cholestasis, where fat-soluble micronutrient malabsorption is known to be an issue (Silva et al. 2015).

Carotenoids, such as zeaxanthin and lycopene, typically have a low bioaccessibility in humans (Biehler and Bohn 2010). However, conversion of raw tomatoes into paste matrix for the bioavailability of lycopene is enhanced due to isomerization of trans-lycopene and cis-lycopene and also due to release from the food matrix (Gärtner et al. 1997; Porrini et al. 1998). In addition, encapsulating lycopene with whey proteins enhances its bioaccessibility to the same level as that of tomato paste. In the same study, zeaxanthin bioavailability is enhanced threefold by homogenizing with hot milk (Richelle et al. 2002). However, in general carotenoids such as lycopene are naturally entrapped in a crystalloid form within the chloroplast, which impedes its liberation and solubilization in the GI tract, while treating the excipients thermally can enhance the migration of carotenoids into the food matrix, thereby increasing its bioaccessibility (Salvia-Trujillo and McClements 2016a, b; Zhang et al. 2016a, c). The bioavailability of carotenoid when co-ingested with excipients is also influenced by the ability of forming micelles through triglycerides (Liu et al. 2015, 2016). This phenomenon was also confirmed in another study where long-chain triglycerides greatly enhanced the β-carotene bioaccessibility in tablet and soft gels compared to medium-chain triglycerides (Laura Salvia-Trujillo and David Julian McClements 2016a, b). Nevertheless, rapid release of carotenoids within gastrointestinal fluids may result in crystallization which would reduce their bioaccessibility (Xia et al. 2015a). However, a proper delivery vehicle should facilitate the solubilization of bioactive compounds without affecting the native physicochemical properties of food matrix. Hence, the type of matrix and bioactive compound would delineate the appropriate type of encapsulation matrix.

7.5 Factors Affecting Nanoencapsulation of Carotenoids

The composition of encapsulating matrix is one of the critical parameters in modulating the structure and properties of carrier matrix. The properties of oil phase including the viscosity, melting point, crystallization form, and hydrophilicity can influence the stability of nanocarriers. The type of nutrient carrier oil phase will regulate the loading capacity such as the crystal structure of the oil phase that hinders the loading capacity of nutrients (Chen et al. 2013). For example, in case of multiple nutrient encapsulations, if maximum nutrient loading capacity is reached, the excess of nutrient molecule may be expelled from the matrix, resulting in chemical degradation and physical instability of the encapsulation matrix. Hence, oil phase screening should be performed to conclude the most appropriate oil phase for the active lipophilic ingredient to be incorporated in nano-lipid carriers. In addition, appropriate surfactant and surfactant composition strongly affect both size distribution and particle size. Thereby, high concentration of surfactant reduces the surface tension and facilitates the particle partition during nanocarrier preparation (McClements 2015).

Utilization of biopolymers and mixed biopolymers for formulation of advanced delivery vehicles or enhancement of existing encapsulation matrix and to enable successive fortification process is a promising technique. In general, encapsulation matrix comprises of one or more biopolymers in its composition. The physicochemical properties of encapsulation matrix base (proteins, polysaccharides, and lipids) as a function of extrinsic and intrinsic molecular key parameters such as concentration, charge amount, size homogeneity, steric formation, pH, temperature, and ionic strength within or between the base composition have been investigated in the past few decades (Jones and McClements 2010). In addition to tailoring of encapsulation matrix for specific feature, it is essential to take consideration of repulsive and attractive forces involved in ingredient interactions. For instance, ingredient interaction specificity and strength are controlled by the presence of salts which induces different attractive interactions. In addition, the magnitude of interaction between food macromolecules is a result of different forces acting between their subunits' nearby macromolecular species (Joye and McClements 2014; McClements et al. 2015). Therefore, intrinsic and extrinsic factors should be considered before incorporating nanoencapsulated carotenoids into food matrices to minimize the loss of carotene functionalities.

7.6 Bioavailability of Encapsulated Carotenoids: Influence of Structural Barriers, Food Structure, and Dietary Factors

Structural Barriers Carotenoids are found in different physical forms (crystals, lipid-dissolved, or lipid crystalline) within the chromoplast substructure and are surrounded by the organelle and cell membranes as well as the cell wall. Both their physical state and location affect liberation from the food matrix. In addition, chromoplast and cell wall structural constituents provide a barrier against carotenoid release from the encapsulation matrix and micelle formation during digestion (Jeffery et al. 2012a; Lemmens et al. 2009; Tydeman et al. 2010). For instance, presence of polysaccharides in the cell wall hinders micelle formulation by encapsulating bile salts and lipids and impeding digestive enzyme interaction with functional molecule for release and absorption. On the other hand, chromoplast structure affects both bioaccessibility and stability of carotenoids by providing a stable environment, resulting in incomplete release and solubilization (Palafox-Carlos et al. 2011). In general intactness of the cell wall and chromoplast substructures constituted an important barrier in carotenoid release; hence, it appears that cell rupture is a prerequisite for carotenoid release and that carotenoids within intact cells are inaccessible during upper gut digestion. Moreover, presence of a low-density cell wall material and high concentration of large plant cells and plastoglobuli (containing the carotenoids) favors carotenoid bioaccessibility (Jeffery et al. 2012a; Jeffery et al. 2012b). However, only few studies have correlated carotenoid bioaccessibility to structural properties of the food matrix, for instance, carotenoid bioaccessibility-pectin properties (Lemmens et al. 2009), carotenoid bioaccessibility-microstructure (Bengtsson et al. 2010; Tydeman et al. 2010), carotenoid bioaccessibility-strength of fiber network (Colle et al. 2010), and carotenoid bioaccessibility-particle diameter (Lemmens et al. 2010). These interpretations clearly specify that differences in chromoplast substructure and cell wall constituents in the matrix are major factors in defining carotenoid bioavailability.

Food Structure The bioavailability and bioaccessibility of encapsulated carotenoids are strongly governed by the concentration and solubility of carotenoids consumed. For instance, due to dissimilarity in molecular hydrophobicity, nonpolar carotenoids present only with triacylglycerol core of oil phase which lacks in generation of micelles, whereas polar carotenoids such as xanthophylls located mainly in the lipid surface of oil droplets can be easily converted into micelles and solubilize the encapsulated nutrients (Rao et al. 2013; Tan et al. 2014c; Xia et al. 2015a, b). This property delivers a relatively high solubility to nonpolar xanthophylls in the bile lipid micelles and increases the bioaccessibility and bioavailability. Enhancing the bioavailability of functional molecules in food matrices is the fundamental objective to increase their bioefficacy. The bioactivity of nanoencapsulated carotenoids largely depends on the size, nature, and shape of the encapsulating matrix (Qian et al. 2012b). Carotenoid bioavailability and the dietary factors affecting it, including processing, and structural barriers are discussed in this section. As contextual information, existing understanding of absorption, metabolism, and transport of carotenoids in the body is explained. The physicochemical characteristics of encapsulated carotenoids in in vitro studies deliver valuable insights; however, these properties in vivo are influenced by various factors other than their basic chemical properties, comprising interactions with surrounding molecules in their microenvironment and may be significantly different from those of free carotenoids. Thus, extrapolations of in vitro results to in vivo conditions should be done with caution (Arunkumar et al. 2013). In addition, the bioavailability of carotenoids in food preparations varies widely; only about 5% of the total carotenoids in whole raw vegetables are absorbed by the intestinal cells, whereas 50% or more of the carotenoids are absorbed from micellar solutions. Therefore, the physical form in which the carotenoid is accessible to intestinal mucosal cells is of critical importance (Saini et al. 2015; Santos and Meireles 2010).

Dietary Factors Nanoencapsulated carotenoids must be absorbed from the intestinal cells, followed by circulation in the bloodstream and delivery to target tissues. Bioavailability of nanoencapsulated carotenoids refers to the fraction of ingested carotenoid that is absorbed and becomes available for storage in the human body or utilization in normal physiological functions (Xia et al. 2015a, b). It is evident from experimental studies that co-ingestion of dietary carotenoids and fat can enhance the bioavailability significantly. This phenomenon is attributed to the fact that solubilization of carotenoid in dietary fat can stimulate provitamin A conversion and retinyl ester digestion through stimulating secretion of bile salts and pancreatic enzymes which helps in the formation of mixed lipid micelles. In addition, dietary fats provide monoglycerides, free fatty acids, and lysophospholipids, serving themselves as components of lipid micelles. Finally, dietary fat co-ingestion with carotenoids stimulates carotenoid and vitamin A absorption by providing the lipid components for intestinal chylomicron assembly (Shafaa et al. 2007).

The in vivo intestinal absorption of encapsulated carotenoids comprises steps: release of encapsulated carotenoids from the food matrix, formation of mixed lipid micelles and solubilization in the lumen, cellular uptake of released carotenoids by mucosal cells, entrapment of absorbed carotenoids from the chylomicrons, and finally secretion of carotenoids and their associated metabolites into the lymph (Shafaa et al. 2007). In the process of carotenoid absorption, basic aspects such as nature of intracellular and luminal factors governing absorption process, absolute absorption efficiency of individual carotenoids, mechanism of intracellular uptake, and transport followed by entrapment into chylomicrons still remain unclarified in the field of science. In addition, it is evident that not only chemical structure of carotenoids but also their isomeric configuration can also influence their absorption. For instance, in tomato 95% of lycopene exist as all-trans isomer, whereas in human plasma, 50% is present in cis-isomer form. But in the gastrointestinal tract due to isomerization bioavailability, cis-isomers of lycopene will enhance and help in crossing the intestinal wall (Richelle et al. 2012).

In the human body, very-low-density lipoproteins are major transporters for free carotenoids, and subsequently, low-density lipoproteins demonstrate maximum concentration of carotenoids in the plasma. Hydrocarbon carotenoids, such as lycopene and α- and β-carotene, are principally positioned in low-density lipoproteins, whereas xanthophylls such as zeaxanthin and lutein are predominantly located in high-density lipoproteins (Saini et al. 2015). Thus, the distribution of food carotenoids among plasma lipoproteins is closely similar to that of cholesterol. In addition, in specific cases, bioavailability of active ingredients can be enhanced or inhibited. Bioactive compounds may interact with each other or their surrounding medium, resulting in the alteration of bioavailability. Enhancers can make a nutrient soluble or prevent their reaction with inhibitors. For instance, as carotenoids are lipophilic, adding minute amounts of dietary fat will result in the improvement of their bioavailability. Inhibitors obstruct nutrient absorption via lowering the solubility and covering the nutrient by binding it to other elements (Noviendri et al. 2011; Santos and Meireles 2010). This phenomenon can be understood based on co-encapsulation strategy used to obtain a synergistic effect between two or more nutraceutical compounds.

Dietary triglyceride enhances carotenoid absorption. For instance, presence of lipid in food matrix promotes the bioavailability of both esterified (Roodenburg et al. 2000) and free lutein (Unlu et al. 2005). In addition, consumption of raw vegetables together with cooked whole eggs increases the bioavailability of zeaxanthin, lutein, lycopene, and α- and β- carotene by three- to eightfold (Kim et al. 2015). Similarly, ingesting of avocado with raw carrot or tomatoes has been demonstrated to increase the bioavailability of β-carotene and its conversion efficiency to vitamin A (Kopec et al. 2014). Dietary fibers could affect carotenoid absorption by several mechanisms: by sequestering micelle components (Eastwood and Mowbray 1976); by inhibiting pancreatic lipase (Hansen 1987), which would decrease carotenoid extraction from lipid droplets (Tyssandier et al. 2001); and by increasing the viscosity of the intestinal content (Gallaher et al. 1993), which would impair the diffusion of carotenoid-rich micelles toward the brush border. In addition, polysaccharide coating such as xanthan gum can hinder the bioaccessibility of β-carotene even at a higher rate of lipid digestion, indicating more monoacylglycerol and free fatty acid formation in small intestinal phase. However, addition of xanthan gum protected the protein-coated lipid droplets by reinforcing the structure to gel network (Park et al. 2018). It is hypothesized that micronutrients can compete with carotenoids regarding their incorporation into mixed micelle and absorption. However, the effect of such competition on long-term carotenoid status is not yet certain (Desmarchelier and Borel 2017).

7.7 Co-encapsulation of Carotenoids with Other Functional Ingredients

It is logical to hypothesize that competition would be observed when multiple carotenoids are co-consumed, as the processes of release from foods, micellarization, and uptake are presumed to be the same. Co-encapsulation is an emerging technology in functional food ingredient encapsulation. There are only few technologies available for co-delivery or co-encapsulation of functional ingredients such as double emulsions and clustered emulsions. The main advantage of co-encapsulation technique is we can deliver two or more nutraceuticals in a single matrix to functional foods, while co-delivering the nutrients, they can show synergistic effect. For instance, double emulsion encapsulation of hydrophobic curcumin and hydrophilic catechin showed a synergistic effect between components and resulted in enhanced stability and bioaccessibility (Aditya et al. 2015). In another study, niosomal formulation of α-tocopherol-curcumin and resveratrol-curcumin co-encapsulation enhanced the radical scavenging ability up to 100% and 40%, respectively (Tavanoet al. 2014b). In a similar study conducted with Tween 60, niosomes containing antioxidants (gallic acid, ascorbic acid, curcumin and quercetin) as single or combination resulted in a synergistic effect between gallic acid-curcumin and ascorbic acid-quercetin molecule co-encapsulation. This result clearly indicates that co-encapsulation of lipophilic and hydrophilic functional molecules can be the future promising novel strategy for nutrient delivery (Tavano et al. 2014a). Brito-Oliveira et al. (2017) studied the co-encapsulation of β-carotene and α-tocopherol in solid lipid microparticles produced with palm stearin and stabilized with hydrolyzed soy protein isolate. They observed that co-encapsulation hindered the degradation rate of β-carotene, and it also prevented the expulsion of functional ingredients during solidification process. In addition, co-encapsulation of astaxanthin with α-tocotrienol in the same liposomal membranes can produce hydrogen bonding of α-tocotrienol with astaxanthin and the intermolecular interaction between the astaxanthin polyene chain and the α-tocotrienol that promotes synergistic antioxidative activity of these compounds toward single oxygen and hydroxyl radicals (Kamezaki et al. 2016). In another study, different fish oil-based lipid nanocarriers with various lutein loadings were formulated, and their physicochemical properties were investigated in detail. The in vitro characterization of lutein-lipid nanocarriers has shown that the fish oil plays important roles in improving the antioxidant capacity. The free- and lutein-loaded nano-lipid carriers have demonstrated the ability to develop a high blocking effect, with a potential to scavenge up to 98% the oxygen free radicals generated into the chemiluminescence system. Most importantly, this comparative study is associated with the main feature of synthesized fish oil-based lipid nanocarriers to exhibit a better in vitro sustained release of lutein as compared to their related nanoemulsions (Lacatusu et al. 2013). Recently, Sotomayor-Gerding et al. (2016) studied the co-delivery of polyunsaturated fatty acid-rich linseed oil and carotenoids (lycopene and astaxanthin) to enhance carotenoid bioaccessibility and oxidative stability of linseed oil. It was observed that lycopene and astaxanthin demonstrated an additive effect and synergistic effect higher (>22×) than synthetic antioxidants.

7.8 Conclusion

Being in the nascent stages of development, nanoencapsulation has a wide spectrum of applications in food industry. It has been proven that there is an increasing interest for the nanoencapsulation of functional molecules such as carotenoids. An overview of carotenoid chemistry, potential application at nanoscale, combined delivery, and their bioavailability has been provided. As it has been seen, factors associated with bioaccessibility of encapsulated carotenoids such as structural barriers in food (cell wall integrity, matrix, and bio-encapsulation), thermal processing, and addition of dietary fat are essential in determining bioavailability. Hence, in-depth interrelated research studies are essential in recognizing the favorable factors to increase the bioavailability of encapsulated carotenoids from different delivery vehicles.

References

Abbas S, Bashari M, Akhtar W, Li WW, Zhang X (2014) Process optimization of ultrasound-assisted curcumin nanoemulsions stabilized by OSA-modified starch. Ultrason Sonochem 21(4):1265–1274

Aditya N, Aditya S, Yang H, Kim HW, Park SO, Ko S (2015) Co-delivery of hydrophobic curcumin and hydrophilic catechin by a water-in-oil-in-water double emulsion. Food Chem 173:7–13

Ahmed K, Li Y, McClements DJ, Xiao H (2012) Nanoemulsion- and emulsion-based delivery systems for curcumin: encapsulation and release properties. Food Chem 132(2):799–807

Altunbas A, Lee SJ, Rajasekaran SA, Schneider JP, Pochan DJ (2011) Encapsulation of curcumin in self-assembling peptide hydrogels as injectable drug delivery vehicles. Biomaterials 32(25):5906–5914

Anarjan N, Mirhosseini H, Baharin BS, Tan CP (2011) Effect of processing conditions on physicochemical properties of sodium caseinate-stabilized astaxanthin nanodispersions. LWT Food Sci Technol 44(7):1658–1665

Arunkumar R, Harish Prashanth KV, Baskaran V (2013) Promising interaction between nanoencapsulated lutein with low molecular weight chitosan: characterization and bioavailability of lutein in vitro and in vivo. Food Chem 141(1):327–337

Augustin MA, Hemar Y (2009) Nano-and micro-structured assemblies for encapsulation of food ingredients. Chem Soc Rev 38(4):902–912

Augustin MA, Sanguansri L (2015) Challenges and solutions to incorporation of nutraceuticals in foods. Annu Rev Food Sci Technol 6:463–477

Banerjee S, Bhattacharya S (2012) Food gels: gelling process and new applications. Crit Rev Food Sci Nutr 52(4):334–346

Bayod E, Tornberg E (2011) Microstructure of highly concentrated tomato suspensions on homogenisation and subsequent shearing. Food Res Int 44(3):755–764

Bayod E, Månsson P, Innings F, Bergenståhl B, Tornberg E (2007) Low shear rheology of concentrated tomato products. Effect of particle size and time. Food Biophys 2(4):146–157

Belščak-Cvitanović A, Bušić A, Barišić L, Vrsaljko D, Karlović S, Špoljarić I, Vojvodić A, Mršić G, Komes D (2016) Emulsion templated microencapsulation of dandelion (Taraxacum officinale L.) polyphenols and β-carotene by ionotropic gelation of alginate and pectin. Food Hydrocoll 57:139–152

Bengtsson A, Brackmann C, Enejder A, Alminger ML, Svanberg U (2010) Effects of thermal processing on the in vitro bioaccessibility and microstructure of β-carotene in orange-fleshed sweet potato. J Agric Food Chem 58(20):11090–11096

Biehler E, Bohn T (2010) Methods for assessing aspects of carotenoid bioavailability. Curr Nutr Food Sci 6(1):44–69

Biehler E, Hoffmann L, Krause E, Bohn T (2011) Divalent minerals decrease micellarization and uptake of carotenoids and digestion products into Caco-2 cells. J Nutr 141(10):1769–1776

Boon CS, McClements DJ, Weiss J, Decker EA (2010) Factors influencing the chemical stability of carotenoids in foods. Crit Rev Food Sci Nutr 50(6):515–532

Borel P, Desmarchelier C, Dumont U, Halimi C, Lairon D, Page D, Sébédio J, Buisson C, Buffière C, Remond D (2016) Dietary calcium impairs tomato lycopene bioavailability in healthy humans. Br J Nutr 116(12):2091–2096

Brito-Oliveira TC, Molina CV, Netto FM, Pinho SC (2017) Encapsulation of Beta-carotene in lipid microparticles stabilized with hydrolyzed soy protein isolate: production parameters, alpha-tocopherol Coencapsulation and stability under stress conditions. J Food Sci 82(3):659–669

Brough C, Williams R (2013) Amorphous solid dispersions and nano-crystal technologies for poorly water-soluble drug delivery. Int J Pharm 453(1):157–166

Bustos-Garza C, Yáñez-Fernández J, Barragán-Huerta BE (2013) Thermal and pH stability of spray-dried encapsulated astaxanthin oleoresin from Haematococcus pluvialis using several encapsulation wall materials. Food Res Int 54(1):641–649

Celik SE, Bekdeser B, Tufan AN, Apak R (2017) Modified radical scavenging and antioxidant activity measurement of β-carotene with β-Cyclodextrins complexation in aqueous medium. Anal Sci 33(3):299–305

Chen X, Chen R, Guo Z, Li C, Li P (2007) The preparation and stability of the inclusion complex of astaxanthin with β-cyclodextrin. Food Chem 101(4):1580–1584

Chen B, McClements DJ, Decker EA (2013) Design of foods with bioactive lipids for improved health. Annu Rev Food Sci Technol 4:35–56

Cheng Y-S, Lu P-M, Huang C-Y, Wu J-J (2017) Encapsulation of lycopene with lecithin and α-tocopherol by supercritical antisolvent process for stability enhancement. J Supercrit Fluids 130:246–252

Chithrani DB, Dunne M, Stewart J, Allen C, Jaffray DA (2010) Cellular uptake and transport of gold nanoparticles incorporated in a liposomal carrier. Nanomedicine 6(1):161–169

Claudie D-M, Bertrand C, Franck T, Marie-Josephe A (2013) Citrus flavanones enhance carotenoid uptake by intestinal Caco-2 cells. Food Funct 4(11):1625–1631

Colle I, Van Buggenhout S, Van Loey A, Hendrickx M (2010) High pressure homogenization followed by thermal processing of tomato pulp: influence on microstructure and lycopene in vitro bioaccessibility. Food Res Int 43(8):2193–2200

Comaposada J, Gou P, Marcos B, Arnau J (2015) Physical properties of sodium alginate solutions and edible wet calcium alginate coatings. LWT-Food Sci Technol 64(1):212–219

Cornacchia L, Roos YH (2011) Stability of β-carotene in protein-stabilized oil-in-water delivery systems. J Agric Food Chem 59(13):7013–7020

Corte-Real J, Iddir M, Soukoulis C, Richling E, Hoffmann L, Bohn T (2016) Effect of divalent minerals on the bioaccessibility of pure carotenoids and on physical properties of gastro-intestinal fluids. Food Chem 197:546–553

Corte-Real J, Desmarchelier C, Borel P, Richling E, Hoffmann L, Bohn T (2018) Magnesium affects spinach carotenoid bioaccessibility in vitro depending on intestinal bile and pancreatic enzyme concentrations. Food Chem 239:751–759

Dasgupta N, Ranjan S, Mundra S, Ramalingam C, Kumar A (2016) Fabrication of food grade vitamin E nanoemulsion by low energy approach, characterization and its application. Int J Food Prop 19(3):700–708

Davidov-Pardo G, Gumus CE, McClements DJ (2016) Lutein-enriched emulsion-based delivery systems: influence of pH and temperature on physical and chemical stability. Food Chem 196:821–827

de Freitas Zômpero RH, López-Rubio A, de Pinho SC, Lagaron JM, de la Torre LG (2015) Hybrid encapsulation structures based on β-carotene-loaded nanoliposomes within electrospun fibers. Colloids Surf B: Biointerfaces 134:475–482

De Prisco A, Mauriello G (2016) Probiotication of foods: a focus on microencapsulation tool. Trends Food Sci Technol 48:27–39

Desmarchelier C, Borel P (2017) Overview of carotenoid bioavailability determinants: from dietary factors to host genetic variations. Trends Food Sci Technol 69:270–280

Eastwood M, Mowbray L (1976) The binding of the components of mixed micelle to dietary fiber. Am J Clin Nutr 29(12):1461–1467

Faisal W, O'driscoll CM, Griffin BT (2010) Bioavailability of lycopene in the rat: the role of intestinal lymphatic transport. J Pharm Pharmacol 62(3):323–331

Fernández-García E, Pérez-Gálvez A (2017) Carotenoid: β-cyclodextrin stability is independent of pigment structure. Food Chem 221:1317–1321

Fernández-García E, Carvajal-Lérida I, Rincon F, Ríos JJ, Perez-Galvez A (2010) In vitro intestinal absorption of carotenoids delivered as molecular inclusion complexes with β-cyclodextrin is not inhibited by high-density lipoproteins. J Agric Food Chem 58(5):3213–3221

Franceschi E, De Cesaro AM, Feiten M, Ferreira SRS, Dariva C, Kunita MH, Rubira AF, Muniz EC, Corazza ML, Oliveira JV (2008) Precipitation of β-carotene and PHBV and co-precipitation from SEDS technique using supercritical CO2. J Supercrit Fluids 47(2):259–269

Gallaher DD, Hassel CA, Lee K-J, Gallaher CM (1993) Viscosity and fermentability as attributes of dietary fiber responsible for the hypocholesterolemic effect in hamsters. J Nutr 123(2):244–252

Gärtner C, Stahl W, Sies H (1997) Lycopene is more bioavailable from tomato paste than from fresh tomatoes. Am J Clin Nutr 66(1):116–122

Gloria NF, Soares N, Brand C, Oliveira FL, Borojevic R, Teodoro AJ (2014) Lycopene and beta-carotene induce cell-cycle arrest and apoptosis in human breast cancer cell lines. Anticancer Res 34(3):1377–1386

Gomes GV, Sola MR, Marostegan LF, Jange CG, Cazado CP, Pinheiro AC, Vicente AA, Pinho SC (2017) Physico-chemical stability and in vitro digestibility of beta-carotene-loaded lipid nanoparticles of cupuacu butter (Theobroma grandiflorum) produced by the phase inversion temperature (PIT) method. J Food Eng 192:93–102

Gómez-Mascaraque LG, Perez-Masiá R, González-Barrio R, Periago MJ, López-Rubio A (2017) Potential of microencapsulation through emulsion-electrospraying to improve the bioaccessibility of β-carotene. Food Hydrocoll 73:1–12

Gruszecki WI, Strzałka K (2005) Carotenoids as modulators of lipid membrane physical properties. Biochim Biophys Acta Mol Basis Dis 1740(2):108–115

Guo Y, Wang X, Shu X, Shen Z, Sun R-C (2012) Self-assembly and paclitaxel loading capacity of cellulose-graft-poly (lactide) nanomicelles. J Agric Food Chem 60(15):3900–3908

Ha TVA, Kim S, Choi Y, Kwak H-S, Lee SJ, Wen J, Oey I, Ko S (2015) Antioxidant activity and bioaccessibility of size-different nanoemulsions for lycopene-enriched tomato extract. Food Chem 178:115–121

Hansen WE (1987) Effect of dietary fiber on pancreatic lipase activity in vitro. Pancreas 2(2):195–198

Havaux M (2014) Carotenoid oxidation products as stress signals in plants. Plant J 79(4):597–606

Hoffman AS (2012) Hydrogels for biomedical applications. Adv Drug Deliv Rev 64:18–23

Jarunglumlert T, Nakagawa K, Adachi S (2015) Influence of aggregate structure of casein on the encapsulation efficiency of β-carotene entrapped via hydrophobic interaction. Food Struct 5:42–50

Jeffery J, Holzenburg A, King S (2012a) Physical barriers to carotenoid bioaccessibility. Ultrastructure survey of chromoplast and cell wall morphology in nine carotenoid-containing fruits and vegetables. J Sci Food Agric 92(13):2594–2602

Jeffery JL, Turner ND, King SR (2012b) Carotenoid bioaccessibility from nine raw carotenoid-storing fruits and vegetables using an in vitro model. J Sci Food Agric 92(13):2603–2610

Jones OG, McClements DJ (2010) Functional biopolymer particles: design, fabrication, and applications. Compr Rev Food Sci Food Saf 9(4):374–397

Joye IJ, McClements DJ (2014) Biopolymer-based nanoparticles and microparticles: fabrication, characterization, and application. Curr Opin Colloid Interface Sci 19(5):417–427

Kamezaki C, Nakashima A, Yamada A, Uenishi S, Ishibashi H, Shibuya N, Hama S, Hosoi S, Yamashita E, Kogure K (2016) Synergistic antioxidative effect of astaxanthin and tocotrienol by co-encapsulated in liposomes. J Clin Biochem Nutr 59(2):100–106

Kandansamy K, Somasundaram PD (2012) Microencapsulation of colors by spray drying-a review. Int J Food Eng 8(2):1–15

Kha TC, Nguyen MH, Roach PD (2010) Effects of spray drying conditions on the physicochemical and antioxidant properties of the Gac (Momordica cochinchinensis) fruit aril powder. J Food Eng 98(3):385–392

Kim DM, Hyun SS, Yun P, Lee CH, Byun SY (2012) Identification of an emulsifier and conditions for preparing stable nanoemulsions containing the antioxidant astaxanthin. Int J Cosmet Sci 34(1):64–73

Kim JE, Gordon SL, Ferruzzi MG, Campbell WW (2015) Effects of egg consumption on carotenoid absorption from co-consumed, raw vegetables. Am J Clin Nutr 102(1):75–83

Kim JE, Ferruzzi MG, Campbell WW (2016) Egg consumption increases vitamin E absorption from co-consumed raw mixed vegetables in healthy Young Men1–3. J Nutr 146(11):2199–2205

Kinder E, Moroz P, Diederich G, Johnson A, Kirsanova M, Nemchinov A, O'Connor T, Roth D, Zamkov M (2011) Fabrication of all-inorganic nanocrystal solids through matrix encapsulation of nanocrystal arrays. J Am Chem Soc 133(50):20488

Kong L, Ziegler GR (2014) Molecular encapsulation of ascorbyl palmitate in preformed V-type starch and amylose. Carbohydr Polym 111:256–263

Kong L, Bhosale R, Ziegler GR (2018) Encapsulation and stabilization of β-carotene by amylose inclusion complexes. Food Res Int 105:446–452

Kopec RE, Cooperstone JL, Schweiggert RM, Young GS, Harrison EH, Francis DM, Clinton SK, Schwartz SJ (2014) Avocado consumption enhances human postprandial provitamin A absorption and conversion from a novel high–β-carotene tomato sauce and from Carrots1,2. J Nutr 144(8):1158–1166

Lacatusu I, Mitrea E, Badea N, Stan R, Oprea O, Meghea A (2013) Lipid nanoparticles based on omega-3 fatty acids as effective carriers for lutein delivery. Preparation and in vitro characterization studies. J Funct Foods 5(3):1260–1269

Lemmens L, Van Buggenhout S, Oey I, Van Loey A, Hendrickx M (2009) Towards a better understanding of the relationship between the β-carotene in vitro bio-accessibility and pectin structural changes: a case study on carrots. Food Res Int 42(9):1323–1330

Lemmens L, Van Buggenhout S, Van Loey AM, Hendrickx ME (2010) Particle size reduction leading to cell wall rupture is more important for the β-carotene bioaccessibility of raw compared to thermally processed carrots. J Agric Food Chem 58(24):12769–12776

Li J-M, Nie S-P (2016) The functional and nutritional aspects of hydrocolloids in foods. Food Hydrocoll 53:46–61

Liaaen-Jensen S, Jensen A (1966) Recent progress in carotenoid chemistry. Prog Chem Fats Other Lipids 8:133–212

Lin N, Huang J, Dufresne A (2012) Preparation, properties and applications of polysaccharide nanocrystals in advanced functional nanomaterials: a review. Nanoscale 4(11):3274–3294

Liu X, Bi J, Xiao H, McClements DJ (2015) Increasing carotenoid bioaccessibility from yellow peppers using excipient emulsions: impact of lipid type and thermal processing. J Agric Food Chem 63(38):8534–8543

Liu X, Bi J, Xiao H, McClements DJ (2016) Enhancement of nutraceutical bioavailability using excipient Nanoemulsions: role of lipid digestion products on bioaccessibility of carotenoids and Phenolics from mangoes. J Food Sci 81(3):N754–N761

Lobo FAT, Silva V, Domingues J, Rodrigues S, Costa V, Falcão D, de Lima Araújo KG (2017) Inclusion complexes of yellow bell pepper pigments with β-cyclodextrin: preparation, characterisation and application as food natural colorant. J Sci Food Agric 98:2665–2671. https://doi.org/10.1002/jsfa.8760

Lohith Kumar D, Sarkar P (2017) Nanoemulsions for nutrient delivery in food. In: Ranjan S, Dasgupta N, Lichtfouse E (eds) Nanoscience in food and agriculture 5. Springer International Publishing, Cham, pp 81–121

Lohith Kumar DH, Sarkar P (2018) Encapsulation of bioactive compounds using nanoemulsions. Environ Chem Lett 16(1):59–70

Mahdavi SA, Jafari SM, Ghorbani M, Assadpoor E (2014) Spray-drying microencapsulation of anthocyanins by natural biopolymers: A review. Dry Technol 32(5):509–518

Marze S (2015) Bioaccessibility of lipophilic micro-constituents from a lipid emulsion. Food Funct 6(10):3218–3227

McClements DJ (2012) Advances in fabrication of emulsions with enhanced functionality using structural design principles. Curr Opin Colloid Interface Sci 17(5):235–245

McClements DJ (2015) Enhancing nutraceutical bioavailability through food matrix design. Curr Opin Food Sci 4:1–6

McClements DJ, Li Y (2010) Structured emulsion-based delivery systems: controlling the digestion and release of lipophilic food components. Adv Colloid Interf Sci 159(2):213–228

McClements DJ, Rao J (2011) Food-grade nanoemulsions: formulation, fabrication, properties, performance, biological fate, and potential toxicity. Crit Rev Food Sci Nutr 51(4):285–330

McClements DJ, Li F, Xiao H (2015) The nutraceutical bioavailability classification scheme: classifying nutraceuticals according to factors limiting their oral bioavailability. Annu Rev Food Sci Technol 6:299–327

Mirza RM (2017) A nanocrystal technology: to enhance solubility of poorly water soluble drugs. J Appl Pharm Res 5(1):1–13

Moffat KL, Marra KG (2004) Biodegradable poly (ethylene glycol) hydrogels crosslinked with genipin for tissue engineering applications. J Biomed Mater Res B Appl Biomater 71(1):181–187

Moraes M, Carvalho JMP, Silva CR, Cho S, Sola MR, Pinho SC (2013) Liposomes encapsulating beta-carotene produced by the proliposomes method: characterisation and shelf life of powders and phospholipid vesicles. Int J Food Sci Technol 48(2):274–282

Muhamad II, Fen LS, Hui NH, Mustapha NA (2011) Genipin-cross-linked kappa-carrageenan/carboxymethyl cellulose beads and effects on beta-carotene release. Carbohydr Polym 83(3):1207–1212

Mun S, Kim Y-R, McClements DJ (2015a) Control of β-carotene bioaccessibility using starch-based filled hydrogels. Food Chem 173:454–461

Mun S, Kim Y-R, Shin M, McClements DJ (2015b) Control of lipid digestion and nutraceutical bioaccessibility using starch-based filled hydrogels: influence of starch and surfactant type. Food Hydrocoll 44:380–389

Nik AM, Corredig M, Wright AJ (2011) Release of lipophilic molecules during in vitro digestion of soy protein-stabilized emulsions. Mol Nutr Food Res 55(S2):S278

Noviendri D, Hasrini RF, Octavianti F (2011) Carotenoids: sources, medicinal properties and their application in food and nutraceutical industry. J Med Plants Res 5(33):7119–7131

Özkan G, Bilek SE (2014) Microencapsulation of natural food colourants. Int J Nutr Food Sci 3(3):145–156

Palafox-Carlos H, Ayala-Zavala JF, González-Aguilar GA (2011) The role of dietary fiber in the bioaccessibility and bioavailability of fruit and vegetable antioxidants. J Food Sci 76(1):R6–R15

Palmero P, Panozzo A, Colle I, Chigwedere C, Hendrickx M, Van Loey A (2016) Role of structural barriers for carotenoid bioaccessibility upon high pressure homogenization. Food Chem 199:423–432

Panozzo A, Lemmens L, Van Loey A, Manzocco L, Nicoli MC, Hendrickx M (2013) Microstructure and bioaccessibility of different carotenoid species as affected by high pressure homogenisation: a case study on differently coloured tomatoes. Food Chem 141(4):4094–4100

Park S, Mun S, Kim Y-R (2018) Effect of xanthan gum on lipid digestion and bioaccessibility of β-carotene-loaded rice starch-based filled hydrogels. Food Res Int 105:440–445

Peng C-H, Chang C-H, Peng RY, Chyau C-C (2010) Improved membrane transport of astaxanthine by liposomal encapsulation. Eur J Pharm Biopharm 75(2):154–161

Pérez-Masiá R, Lagaron JM, Lopez-Rubio A (2015) Morphology and stability of edible lycopene-containing micro-and nanocapsules produced through electrospraying and spray drying. Food Bioprocess Technol 8(2):459–470

Porrini M, Riso P, Testolin G (1998) Absorption of lycopene from single or daily portions of raw and processed tomato. Br J Nutr 80(04):353–361

Poulaert M, Borel P, Caporiccio B, Gunata Z, Dhuique-Mayer C (2012) Grapefruit juices impair the bioaccessibility of β-carotene from orange-fleshed sweet potato but not its intestinal uptake by Caco-2 cells. J Agric Food Chem 60(2):685–691

Qian C, Decker EA, Xiao H, McClements DJ (2012a) Inhibition of β-carotene degradation in oil-in-water nanoemulsions: influence of oil-soluble and water-soluble antioxidants. Food Chem 135(3):1036–1043

Qian C, Decker EA, Xiao H, McClements DJ (2012b) Nanoemulsion delivery systems: influence of carrier oil on β-carotene bioaccessibility. Food Chem 135(3):1440–1447

Qian C, Decker EA, Xiao H, McClements DJ (2012c) Physical and chemical stability of β-carotene-enriched nanoemulsions: influence of pH, ionic strength, temperature, and emulsifier type. Food Chem 132(3):1221–1229

Quintanilla-Carvajal MX, Camacho-Díaz BH, Meraz-Torres LS, Chanona-Pérez JJ, Alamilla-Beltrán L, Jimenéz-Aparicio A, Gutiérrez-López GF (2010) Nanoencapsulation: a new trend in food engineering processing. Food Eng Rev 2(1):39–50

Qv X-Y, Zeng Z-P, Jiang J-G (2011) Preparation of lutein microencapsulation by complex coacervation method and its physicochemical properties and stability. Food Hydrocoll 25(6):1596–1603

Rajabi H, Ghorbani M, Jafari SM, Sadeghi Mahoonak A, Rajabzadeh G (2015) Retention of saffron bioactive components by spray drying encapsulation using maltodextrin, gum Arabic and gelatin as wall materials. Food Hydrocoll 51:327–337

Rao J, Decker EA, Xiao H, McClements DJ (2013) Nutraceutical nanoemulsions: influence of carrier oil composition (digestible versus indigestible oil) on β-carotene bioavailability. J Sci Food Agric 93(13):3175–3183

Richelle M, Bortlik K, Liardet S, Hager C, Lambelet P, Baur M, Applegate LA, Offord EA (2002) A food-based formulation provides lycopene with the same bioavailability to humans as that from tomato paste. J Nutr 132(3):404–408

Richelle M, Lambelet P, Rytz A, Tavazzi I, Mermoud A-F, Juhel C, Borel P, Bortlik K (2012) The proportion of lycopene isomers in human plasma is modulated by lycopene isomer profile in the meal but not by lycopene preparation. Br J Nutr 107(10):1482–1488

Rocha-Selmi GA, Favaro-Trindade CS, Grosso CR (2013a) Morphology, stability, and application of lycopene microcapsules produced by complex coacervation. J Chem 2013:1–7

Rocha-Selmi GA, Theodoro AC, Thomazini M, Bolini HM, Favaro-Trindade CS (2013b) Double emulsion stage prior to complex coacervation process for microencapsulation of sweetener sucralose. J Food Eng 119(1):28–32

Roodenburg AJ, Leenen R, van het Hof KH, Weststrate JA, Tijburg LB (2000) Amount of fat in the diet affects bioavailability of lutein esters but not of α-carotene, β-carotene, and vitamin E in humans. Am J Clin Nutr 71(5):1187–1193

Rösler A, Vandermeulen GWM, Klok H-A (2012) Advanced drug delivery devices via self-assembly of amphiphilic block copolymers. Adv Drug Deliv Rev 64:270–279

Saini RK, Nile SH, Park SW (2015) Carotenoids from fruits and vegetables: chemistry, analysis, occurrence, bioavailability and biological activities. Food Res Int 76:735–750

Sáiz-Abajo M-J, González-Ferrero C, Moreno-Ruiz A, Romo-Hualde A, González-Navarro CJ (2013) Thermal protection of β-carotene in re-assembled casein micelles during different processing technologies applied in food industry. Food Chem 138(2):1581–1587

Salvia-Trujillo L, McClements DJ (2016a) Enhancement of lycopene bioaccessibility from tomato juice using excipient emulsions: influence of lipid droplet size. Food Chem 210:295–304

Salvia-Trujillo L, McClements DJ (2016b) Improvement of β-carotene bioaccessibility from dietary supplements using excipient Nanoemulsions. J Agric Food Chem 64(22):4639–4647

Salvia-Trujillo L, Qian C, Martín-Belloso O, McClements D (2013) Modulating β-carotene bioaccessibility by controlling oil composition and concentration in edible nanoemulsions. Food Chem 139(1):878–884

Santos DT, Meireles MAA (2010) Carotenoid pigments encapsulation: fundamentals, techniques and recent trends. Open Chem Eng J 4(1):42–50

Sari T, Mann B, Kumar R, Singh R, Sharma R, Bhardwaj M, Athira S (2015) Preparation and characterization of nanoemulsion encapsulating curcumin. Food Hydrocoll 43:540–546

Sarkar P, Lohith Kumar DH, Dhumal C, Panigrahi SS, Choudhary R (2015) Traditional and ayurvedic foods of Indian origin. J Ethnic Foods 2(3):97–109

Shafaa MWI, Diehl HA, Socaciu C (2007) The solubilisation pattern of lutein, zeaxanthin, canthaxanthin and β-carotene differ characteristically in liposomes, liver microsomes and retinal epithelial cells. Biophys Chem 129(2–3):111–119

Silva DF, Favaro-Trindade CS, Rocha GA, Thomazini M (2012) Microencapsulation of lycopene by gelatin–pectin complex coacervation. J Food Process Preserv 36(2):185–190

Silva M, Gomes S, Peixoto A, Torres-Ramalho P, Cardoso H, Azevedo R, Cunha C, Macedo G (2015) Nutrition in chronic liver disease. GE Port J Gastroenterol 22(6):268–276

Sotomayor-Gerding D, Oomah BD, Acevedo F, Morales E, Bustamante M, Shene C, Rubilar M (2016) High carotenoid bioaccessibility through linseed oil nanoemulsions with enhanced physical and oxidative stability. Food Chem 199:463–470

Soukoulis C, Bohn T (2018) A comprehensive overview on the micro-and nano-technological encapsulation advances for enhancing the chemical stability and bioavailability of carotenoids. Crit Rev Food Sci Nutr 58(1):1–36

Soukoulis C, Cambier S, Hoffmann L, Bohn T (2016) Chemical stability and bioaccessibility of β-carotene encapsulated in sodium alginate o/w emulsions: impact of Ca2+ mediated gelation. Food Hydrocoll 57:301–310

Svelander CA, Lopez-Sanchez P, Pudney PD, Schumm S, Alminger MA (2011) High pressure homogenization increases the in vitro bioaccessibility of α-and β-carotene in carrot emulsions but not of lycopene in tomato emulsions. J Food Sci 76(9):H215

Tan C, Xia S, Xue J, Xie J, Feng B, Zhang X (2013) Liposomes as vehicles for lutein: preparation, stability, liposomal membrane dynamics, and structure. J Agric Food Chem 61(34):8175–8184

Tan C, Xue J, Abbas S, Feng B, Zhang X, Xia S (2014a) Liposome as a delivery system for carotenoids: comparative antioxidant activity of carotenoids as measured by ferric reducing antioxidant power, DPPH assay and lipid peroxidation. J Agric Food Chem 62(28):6726–6735

Tan C, Xue J, Lou X, Abbas S, Guan Y, Feng B, Zhang X, Xia S (2014b) Liposomes as delivery systems for carotenoids: comparative studies of loading ability, storage stability and in vitro release. Food Funct 5(6):1232–1240

Tan C, Zhang Y, Abbas S, Feng B, Zhang X, Xia S (2014c) Modulation of the carotenoid bioaccessibility through liposomal encapsulation. Colloids Surf B: Biointerfaces 123:692–700

Tan C, Feng B, Zhang X, Xia W, Xia S (2016) Biopolymer-coated liposomes by electrostatic adsorption of chitosan (chitosomes) as novel delivery systems for carotenoids. Food Hydrocoll 52:774–784

Tavano L, Muzzalupo R, Picci N, de Cindio B (2014a) Co-encapsulation of antioxidants into niosomal carriers: gastrointestinal release studies for nutraceutical applications. Colloids Surf B: Biointerfaces 114:82–88

Tavano L, Muzzalupo R, Picci N, de Cindio B (2014b) Co-encapsulation of lipophilic antioxidants into niosomal carriers: percutaneous permeation studies for cosmeceutical applications. Colloids Surf B: Biointerfaces 114:144–149

Trentin A, De Lamo S, Güell C, López F, Ferrando M (2011) Protein-stabilized emulsions containing beta-carotene produced by premix membrane emulsification. J Food Eng 106(4):267–274

Trivedi R, Kompella UB (2010) Nanomicellar formulations for sustained drug delivery: strategies and underlying principles. Nanomedicine 5(3):485–505

Tydeman EA, Parker ML, Wickham MS, Rich GT, Faulks RM, Gidley MJ, Fillery-Travis A, Waldron KW (2010) Effect of carrot (Daucus carota) microstructure on carotene bioaccessibility in the upper gastrointestinal tract. 1. In vitro simulations of carrot digestion. J Agric Food Chem 58(17):9847–9854

Tyssandier V, Lyan B, Borel P (2001) Main factors governing the transfer of carotenoids from emulsion lipid droplets to micelles. Biochim Biophys Acta Mol Cell Biol Lipids 1533 (3):285–292

Unlu NZ, Bohn T, Clinton SK, Schwartz SJ (2005) Carotenoid absorption from salad and salsa by humans is enhanced by the addition of avocado or avocado oil. J Nutr 135(3):431–436

Vishwanathan R, Wilson TA, Nicolosi RJ (2009) Bioavailability of a nanoemulsion of lutein is greater than a lutein supplement. Nano Biomed Eng 1(1):38–49

Xavier AAO, Mercadante AZ, Garrido-Fernández J, Pérez-Gálvez A (2014) Fat content affects bioaccessibility and efficiency of enzymatic hydrolysis of lutein esters added to milk and yogurt. Food Res Int 65:171–176

Xia Z, McClements DJ, Xiao H (2015a) Influence of physical state of β-carotene (Crystallized versus solubilized) on bioaccessibility. J Agric Food Chem 63(3):990–997

Xia S, Tan C, Zhang Y, Abbas S, Feng B, Zhang X, Qin F (2015b) Modulating effect of lipid bilayer–carotenoid interactions on the property of liposome encapsulation. Colloids Surf B: Biointerfaces 128:172–180

Xu D, Wang X, Jiang J, Yuan F, Decker EA, Gao Y (2013) Influence of pH, EDTA, α-tocopherol, and WPI oxidation on the degradation of β-carotene in WPI-stabilized oil-in-water emulsions. LWT-Food Sci Technol 54(1):236–241

Yang Y, Guo Y, Sun R, Wang X (2016) Self-assembly and β-carotene loading capacity of hydroxyethyl cellulose-graft-linoleic acid nanomicelles. Carbohydr Polym 145:56–63

Yin L-J, Chu B-S, Kobayashi I, Nakajima M (2009) Performance of selected emulsifiers and their combinations in the preparation of β-carotene nanodispersions. Food Hydrocoll 23(6):1617–1622

Yuan Y, Gao Y, Zhao J, Mao L (2008a) Characterization and stability evaluation of β-carotene nanoemulsions prepared by high pressure homogenization under various emulsifying conditions. Food Res Int 41(1):61–68

Yuan C, Jin Z, Xu X, Zhuang H, Shen W (2008b) Preparation and stability of the inclusion complex of astaxanthin with hydroxypropyl-β-cyclodextrin. Food Chem 109(2):264–268

Yuan C, Jin Z, Xu X (2012) Inclusion complex of astaxanthin with hydroxypropyl-β-cyclodextrin: UV, FTIR, 1H NMR and molecular modeling studies. Carbohydr Polym 89(2):492–496

Zhang R, Zhang Z, Kumosani T, Khoja S, Abualnaja KO, McClements DJ (2016a) Encapsulation of β-carotene in Nanoemulsion-based delivery systems formed by spontaneous emulsification: influence of lipid composition on stability and bioaccessibility. Food Biophys 11(2):154–164

Zhang Z, Zhang R, McClements DJ (2016b) Encapsulation of β-carotene in alginate-based hydrogel beads: impact on physicochemical stability and bioaccessibility. Food Hydrocoll 61:1–10

Zhang R, Zhang Z, Zou L, Xiao H, Zhang G, Decker EA, McClements DJ (2016c) Impact of lipid content on the ability of excipient emulsions to increase carotenoid bioaccessibility from natural sources (raw and cooked carrots). Food Biophys 11(1):71–80

Chapter 8
Nanomaterials in Agricultural Research: An Overview

Deepa Garg and Devendra K. Payasi

Contents

8.1 Introduction 244
8.2 Nanomaterials 246
  8.2.1 Natural Nanoparticle/Organic Nanomaterials 246
  8.2.2 Inorganic Nanomaterials 246
8.3 Applications of Nanomaterials in Agricultural Production and Protection 247
  8.3.1 Seed Science and Technology 247
  8.3.2 Crop Improvement 248
  8.3.3 Crop Biotechnology 250
  8.3.4 Plant Disease Diagnostics and Management 252
  8.3.5 Insect Pest Management 256
  8.3.6 Nanomolecules in Recycling Agricultural Waste 259
  8.3.7 Nanofertilizers and Nanocomplex 261
  8.3.8 Nanotechnologies for Water Quality and Availability 263
  8.3.9 Phytochemicals and Essential Oils 265
  8.3.10 Nanotech Delivery Systems for Pests and Nutrients 265
  8.3.11 Nanosensors/Nanobiosensors in Agri-food Production 265
  8.3.12 Plant Hormones 266
  8.3.13 Quality of Agricultural Food Products 267
  8.3.14 Bioengineering 267
8.4 Conclusion 267
References 269

Abstract New emerging technologies are often applied to improve the yield and quality of crops. Recent advancement in science and technology in the field of agricultural research has led to create unique properties targeted toward specific application in crop improvement. Nano-agriculture involves the employment of nanoparticles in agriculture. The emergence of nanotechnology and the development of nanodevices and nanomaterials can boost agricultural production by enhanced

---

D. Garg
Department of Biotechnology, Kurukshetra University, Kurukshetra, Haryana, India

D. K. Payasi (✉)
Jawaharlal Nehru Krishi Vishwa Vidyalaya, Regional Agricultural Research Station, Sagar, Madhya Pradesh, India

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_8

reactivity due to enhanced solubility, greater proportion of surface atoms relative to the interior of structure, unique magnetic/optical properties, electronic states, and catalytic reactivity that differ from equivalent bulk materials. These materials would release pesticides or fertilizers at a specific time and targeted location. Nanoparticles tagged to agrochemicals or other substances could reduce the damage to other plant tissues and the amount of chemical released into the environment. Between 1961 and 1999, global production outstripped population growth, but this was achieved partly through a 12% increase in the global area of cropland and a 10% increase in the area of permanent posture. During the same period, the overall productivity grew to 106%; however, this was linked to a 97% rise in the area of land under irrigation and 638%, 203%, and 854% increases, respectively, in the use of nitrogenous and phosphate fertilizers and production of pesticides. The situation could be gauged from data for the irrigated farming regions of the country, where the return of grain yield per kilogram of nutrient use was reduced from 13.4 kg in 1970 to 3.7 kg in 2015. The positive morphological effects of nanomaterials include enhanced germination percent and rate, whole plant architecture including root and shoot length and their ratio, biomass of seedlings, and harvest index of the plants. Application of nanomaterials in agricultural research holds the promise of controlled release of agrochemicals and site-targeted delivery of various useful macromolecules needed for improved plant disease resistance, efficient utilization of nutrients, and enhanced plant growth.

Keywords Agriculture · Nanomaterials · Nanoparticles · Nanosensor · Smart delivery system

8.1 Introduction

The world's population is increasing at an alarming rate and is expected to reach eight billion people by 2025 and nine billion by the end of that year, and it is widely recognized that global agricultural productivity must increase to feed a rapidly growing population (Sekhon 2014). Population growth and the resultant development of large high-density urban populations, together with parallel global industrialization, have placed major pressures on our environment, potentially threatening environmental sustainability and food security. This has resulted in global warming and the buildup of chemical and biological contaminants throughout the biosphere, but most notably in soils and sediments (Yazdani et al. 2007). Agriculture is the backbone of most of the developing countries. The agricultural sector is facing various global challenges, environmental issues, urbanization, sustainable use of resources, and accumulation of pesticides and fertilizers. Many countries including India have identified the potential of nanotechnology in the field of agriculture such as precision farming, smart delivery systems, food industry, food processing, packaging, food safety, etc. Traditional farming techniques have attained saturation and are neither able to increase the productivity nor able to restore ecosystem damaged by existing technologies (Tripathi et al. 2018). Nanotechnology has the potential to revolutionize the agriculture with new tools for the rapid disease detection and their treatments, enhancing the ability of plants to absorb nutrients, increasing the efficiency of pesticides and weedicides. Nanotechnology is recognized by the European Commission as one of its six “Key Enabling Technologies” that contribute to sustainable competitiveness and growth in several industrial sectors. The current challenges of sustainability, food security, and climate change are engaging researchers in exploring the field of nanotechnology as a new source of key improvements for the agricultural sector. On the one hand, industry experts stress that agricultural nanotechnology does not demonstrate a sufficient economic return to counterbalance the high initial production investments (Parisi et al. 2015). In contrary, nanotechnology provides new agrochemical agents and new delivery mechanisms to improve crop productivity, and it promises to reduce pesticide use. Nanosensors/nanobiosensors have been applied in crop protection for the identification of disease and residues of agrochemicals, as well as nanodevices for the genetic manipulation of plants, plant disease diagnostics, animal health, and animal breeding. Precision farming technique could further improve yields without affecting soil and water, reduce nitrogen loss due to leaching and emission, and enhance nutrients’ long-term incorporation by soil microbes.

The new chemical and/or physical properties of nanoscale particles provide useful function that are being rapidly exploited in crop improvement, plant biotechnology, genetic engineering, nanofertilizer production, nanopesticide formulations, postharvest management, etc. These promising developments in agricultural sectors strongly need continuous innovations for increasing global food security and climate change challenges (Parisi et al. 2015). Nanomaterials are also used in nanoparticle-mediated gene or DNA transfer into plants for the development of resistant cultivars, crop improvement, food processing and storage, and nano-feed additives and increasing a product’s shelf-life (Sekhon 2014). Nanomaterials are used in agricultural products across the supply chain including in (i) chemicals and fertilizers, (ii) feed and supplements for farm animals, (iii) machinery, and storage facilities.

The development of nanotechnology in conjugation with biotechnology has significantly expanded the application domain of nanomaterials in various fields of agricultural products. A variety of carbon-based, metal, and metal oxide nanomaterials (Nair et al. 2010) are being developed. Types include single-walled and multi-walled carbon nanotubes (SWCNT/MWCNT), magnetized iron (Fe) nanoparticles, aluminum (Al), copper (Cu), gold (Au), silver (Ag), silica (Si), zinc (Zn), nanoparticles and nanooxide (ZnO), titanium dioxide (TiO_2), and cerium oxide (Ce_2O_3). General applications of these materials are found in water purification, wastewater treatment, environmental remediation, and food processing and packaging (Qureshi et al. 2009; Lee et al. 2010; Zambrano-Zaragoza et al. 2011; Bradley et al. 2011; Khot et al. 2012). The majority of applications in these areas have focused on the significance of nanomaterials for improving efficiency and productivity. These materials are also used in agricultural production and crop protection (Bouwmeester et al. 2009; Nair et al. 2010; Sharon et al. 2010; Emamifar et al. 2010; Khot et al. 2012).

8.2 Nanomaterials

Any form of a material that has one or more dimensions in the nanoscale is known as nanomaterial. The materials that are lesser than 100 nm in, at least, one dimension are referred to as nanomaterials. Hence, nanoparticles can be zero-dimensional (all dimensions are at nanoscales), one-dimensional (fine rod-shaped), two-dimensional (ultrathin films), or three-dimensional (of any shape) based on their manipulation of matter (Bernhardt et al. 2008). Nair et al. (2010) reviewed that during the last two decades, a significant amount of research has been conducted in nanotechnology focusing on their applications in electronics, energy, medicine, and life sciences including plant sciences.

8.2.1 Natural Nanoparticle/Organic Nanomaterials

Naturally occurring nanoparticles (such as nanoclay, tomato carotenoid lycopene, materials derived from soil organic matter, lipoprotein, exosomes, magnetosomes, viruses, and ferritin) have diverse structures with wide-ranging biological roles. They are often biocompatible and have reproducible structures.

8.2.2 Inorganic Nanomaterials

Among inorganic materials, metal oxide nanoparticles such as ZnO, AgO, TiO_2, and MgO, photocatalytic (ZnO, TiO_2) and microbiocidal (MgO and AgO), are used for pesticide detection and degradation. Organic materials such as carbon nanotubes, lipids, and polymers are versatile and have multiple applications in agricultural industries. Engineered nanoparticles can be categorized into five types like carbon-based NPs, metal-based NPs, magnetic nanoparticles, dendrimers, and composite nanoparticles. Carbon-based nanoparticles include fullerene (C_{70}), fullerol ($C_{60}(OH)_{20}$), single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and single-walled carbon nanohorns (SWCNHs), while metal-based nanoparticles include gold (Au)-, silver (Ag)-, copper (Cu)-, and iron (Fe)-based nanomaterials. In addition, the different types of metal oxide-based nanoparticles like TiO_2, CeO_2, FeO, Al_2O_3, and ZnO are extensively studied in agriculture and medical sciences. Magnetic nanoparticles can be manipulated using a magnetic field, and such particles commonly consist of iron, cobalt, and nickel and their compounds. Among the different magnetic nanoparticles, when ferrite (an iron oxide (Fe_2O_3)) particles become smaller than 128 nm, they become superparamagnetic. The techniques for making nanoparticles involved either a top-down approach or a bottom-up approach. In the top-down approach, size reduction is achieved by various chemical and physical treatments such as milling, high-pressure homogenization, and sonication, while in bottom-up synthesis, the nanostructured building blocks of nanoparticles are formed first and then assembled to produce the final particle.

8.3 Applications of Nanomaterials in Agricultural Production and Protection

8.3.1 Seed Science and Technology

Seed is the most important input determining crop productivity. Use of nanomolecules may improve the germination and seedling vigor of the crops. A group of researchers is working on use of metal oxide nanoparticles and carbon nanotube to improve the germination under rainfed condition. Khodakovskaya et al. (2009) reported the use of carbon nanotube for improving germination of tomato seeds through better permeation of moisture. Results indicated that the carbon nanotubes serve as a tool to increase water permeability by penetration of seed coat and act as passage to channelize the water from the substrate into the seeds and facilitate seed germination, which can be exploited in rainfed agriculture ecosystem. In recent years, various researchers have studied the effects of nanomaterials on plant germination and growth with a goal to promote its use for agricultural applications. Lu et al. (2002) observed that SiO_2 and TiO_2 nanoparticles positively impact seed germination in soybean and spinach by increasing nitrate reductase and enhancing the uptake and utilization of water and nutrients. Zheng et al. (2005) studied the effects of nano- and nao-nano-TiO_2 on the growth of naturally aged spinach seeds. It was reported that nano-TiO_2-treated seed produced plants that had 73% more dry weight, three times higher photosynthetic rate, and 45% increase in chlorophyll formation compared to control. Lin and Xing (2007) evaluated phytotoxicity of nanomaterials (MWCNTs, Al_2O_3, ZnO, Al, and Zn) and its impact on germination rates in radish, rape canola, ryegrass, lettuce, corn, and cucumber. They conferred the hypothesis that the higher concentrations (2000 mg/L) of nano-sized Zn (35) and ZnO (20 nm) inhibited the germination in ryegrass and corn, respectively. Suriyaprabha et al. (2012) studied that better nutrient availability to maize seeds on supplementation with SiO_2 nanoparticles expresses positive effects on the germination rate. Siddiqui and Al-Whaibi (2014) reported that silica nanoparticles (SiO_2 NPs) at relatively lower concentrations improved seed germination in tomato.

Upadhyaya et al. (2015) reported that zinc nanoparticles showed significant physiological effect on rice. Zn nanoparticles promote plant growth by increasing more length, biomass, and relative water contact in root and shoot of Zn nanoparticle-treated plants relative to control. Beneficial effects of lower concentrations of zinc oxide nanoparticles on seed germination have been observed in a variety of plant species as peanut (Prasad et al. 2012), soybean (Sedghi et al.

2013), onion (Raskar and Laware 2014), and wheat (Ramesh et al. 2014). ZnO nanoparticles showed differential effects when tested on cucumber, alfalfa, and tomato, with only the former exhibiting enhancement in germination as reported by De la Rosa et al. (2013). Ibrahim, E. A (2016) reported seed priming as a technique that partially hydrates seeds in natural or synthetic compounds under specific environment to a point where germination-related metabolic processes begin, but radicle emergence does not occur. Seed priming has been found to be useful for enhancing seed quality, seedling establishment, and crop yields as well as increasing tolerance to environmental stresses. Seed priming can improve the germination of weak, damaged, or aged seeds or even under adverse environment. Horii et al. (2007) and Hussain et al. (2015) studied a number of commonly used priming agents including polyethylene glycol, inorganic salts, nutrients, and plain water. However, different priming solutions have different properties and effectiveness, and optimization of priming agents is required for each crop species. Therefore, there is a growing need to develop new priming agents to enhance seed germination of various crop plants. Chen and Arora (2013) reported that in commercial agriculture, rapid and uniform seed germination and seedling emergence are important determinants of successful stand establishment. Germination begins with water uptake by the mature dry seed (imbibition) and terminates with the elongation of the embryonic axis, usually the radicle, through the seed envelope, which has, as a consequence, the protrusion of the root and later of the shoot. Mahakham et al. (2017) reviewed that in recent years, several metal-based nanoparticles (e.g., AgNPs, AuNPs, CuNPs, FeNPs, FeS_2NPs, TiO2NPs, ZnNPs, ZnONPs) and carbon-based NPs (e.g., fullerene and carbon nanotubes) have been used as seed pretreatment agents for promoting seed germination, seedling growth, and stress tolerance in some crop plants. Among these studies, only a few researchers have used the seed priming strategy, in which seeds must be re-dried to their original moisture content before sowing. Thus, the mechanism behind seed nanopriming would be different from that of pre-sowing seed treatment without drying seeds.

Nonetheless, future research on nanomaterials for plant germination and growth should address some of the following challenges as reported by Nair et al. (2010): (1) unpredictability in reaction of nanomaterials to different plants, (2) phytotoxicity due to higher concentrations, and (3) reduced intake and photosynthesis of plant due to larger nanomaterials (Table 8.1).

8.3.2 Crop Improvement

Nanotechnology has also shown its ability in modifying the genetic constitution of crop plants, thereby helping in further improvement of crop plants. Mutations – both natural and induced – have long since played an important role in crop improvement. Instead of using certain chemical compounds like EMS and MMS and physical mutagens like X-ray, gamma ray, etc. for conventional induced mutation studies, nanomolecules showed a new dimension in mutation research. A variety of

Table 8.1 List of nanoparticles used to study the effect of growth attributes of crop plants

Nanoparticles used in the study	Crop plant	Effect on growth parameters	References
MWCNTs	Wheat	Root growth (+ve)	Wang et al. (2012)
Co_3O_4	Radish	Root elongation (+ve)	Wu et al. (2012)
CNTs	Wheat	Root growth (+ve)	Wang et al. (2012)
Zn	Radish, rape seed, rye, lettuce, corn, cucumber	Root length (−ve)	Lin and Xing (2007)
MWCNTs	Rye	Root length (+ve)	Lin and Xing (2007)
ZnO	Radish, rape seed, rye, lettuce, corn, cucumber	Root growth (−ve)	Lin and Xing (2007)
Cu	Wheat	Root (−ve)	Lee et al. (2008)
Al_2O_3	Corn, cucumber, cucumber, carrot, cabbage	Root growth (−ve); Root length (−ve)	Yang and Watts (2005)
CNTs	Tomato	Reduction in root	Canas et al. (2008)
ZnO	Corn	Root growth (−ve)	Stampoulis et al. (2009)
Ag	Rice	Shoot growth (−ve)	Mirzajani et al. (2013)
ZnO	Cluster bean	Shoot growth (+ve)	Raliya and Tarafdar (2013)
CeO_2	Corn, alfalfa, soybean	Shoot growth (+ve)	Lopez-Moreno et al. (2010)
$SiO_2 + TiO_2$	Soybean	Shoot growth (+ve)	Lu et al. (2002)
ZnO	Peanut	Root growth (+ve)	Prasad et al. (2012)
Cu	Mung bean *(Vigna radiata)*	Shoot growth (−ve)	Lee et al. (2008)
CNTs	Tomato	Seedling growth (+ve)	Morla et al. (2011)
Ag	Barley, flax, rye	Shoot length (−ve)	El-Temsah and Joner (2010)
MWCNTs	Tobacco	Growth rate (+ve)	Khodakovskaya et al. (2012)
SiO_2	Maize	Growth parameters (+ve)	Suriyaprabha et al. (2012)
TiO_2	Wheat	Root elongation (+ve)	Larue et al. (2012)
CNTs	Alfalfa, wheat	Root elongation (+ve)	Miralles et al. (2012)
SWCNTs	Onion, cucumber	Root elongation (+ve)	Canas et al. (2008)
TiO_2	Spinach	Plant growth (+ve)	Yang et al. (2006)
CNTs	Indian mustard, mung bean	Seedling growth (+ve)	Mondal et al. (2011)
SiO_2 and TiO_2	Soybean	Plant growth (+ve)	Lu et al. (2002)

nanomaterials, mostly metal-based nanomaterials and carbon-based nanomaterials, have been exploited for their absorption, translocation, accumulation, and effects on growth and development of crop plants (Nair et al. (2010); Rico et al. (2011). The positive morphological effects included enhanced germination percentage and rate, length of root and shoot, their ratio, and vegetative biomass of seedlings in many crop plants, including corn, wheat, ryegrass, alfalfa, soybean, rape, tomato, radish, lettuce, spinach, onion, pumpkin, cucumber, etc. Agrawal and Rathore (2014) reported the enhancement of photosynthetic activity and nitrogen metabolism by metal-based nanomaterials in a few crops including soybean: magnetic nanoparticles coated with tetramethylammonium hydroxide led to an increase in chlorophyll-a level in maize. In Thailand, Chiang Mai University's Nuclear Physics Laboratory has come up with a new white-grained rice variety from a traditional purple-colored rice variety called *Khao Kam* through the usage of nanomolecule by drilling a nano-sized hole through the wall and membrane of a rice cell in order to insert a nitrogen atom. The hole is drilled using a particle beam, and the nitrogen atom is shot through the hole to stimulate rearrangement of the rice's DNA. This newly derived organism through the change at the atomic level is designated as "atomically modified organisms" (Mishra et al. 2013).

8.3.3 Crop Biotechnology

Chemists have successfully crafted three-dimensional molecular structures, a breakthrough that unites biotechnology and nanotechnology. They made DNA crystals by producing synthetic DNA sequences that can self-assemble into a series of three-dimensional triangle-like patterns. The DNA crystals have "sticky ends" or small cohesive sequences that can attach to another molecule in an organized fashion. When multiple helices are attached through single-stranded sticky ends, there would be a latticelike structure that extends in six different directions, forming a three-dimensional crystal. This technique could be applied in improving important crops by organizing and linking carbohydrates, lipids, proteins, and nucleic acids to these crystals. Use of nano-sized materials as systems for delivery of genetic material into living cells is a new and promising approach. Nanoparticles can serve as "magic bullets," containing herbicides, chemicals, or genes, which target particular plant parts to release their content. Nanocapsules can enable effective penetration of herbicides through cuticles and tissues, allowing slow and constant release of the active substances. Recent data showed that carbon-based, metal-based, composite, and polymer nanoparticles have a potential to carry nucleic acids into plant cells. The unique ability of nanomaterials to penetrate plant cell wall and move inside the cell in a fast manner can open ways for improvement of a number of transformation techniques including particle bombardment. However, experimental attempts to use nanomaterials as carries of DNA/RNA *in planta* are rare. Chemists at the Iowa State

University have utilized a 3 nm mesoporous silica nanoparticle in delivering DNA and chemicals into isolated plant cells. Mesoporous silica nanoparticles are chemically coated and serve as containers for the genes delivered into the plants. The coating triggers the plant to take the particles through the cell walls, where the genes are inserted and activated in a precise and controlled manner, without any toxic side or aftereffects. This technique has been applied to introduce DNA successfully to tobacco and corn plants (Mishra et al. 2013). The existence of cell wall is making delivery of DNA and RNA into plant cells more difficult. Traditionally, the cell wall barrier can be overcome in plants by removal of the cell wall (Ochatt 2013), infection by *Agrobacterium* or through particle bombardment of cells (Taylor and Fauquet 2002). The advantages of the use of nanomaterials for plant transformation were described by researchers led by Kan Wang and Victor S-Y Lin (Torney et al. 2007). They demonstrated that mesoporous silica nanoparticle system (MSNS) was capable of delivering DNA and chemicals into plant cells and plant leaves (Torney et al. 2007). Gold nanoparticles also may provide an attractive tool for delivery of proteins and genes to living organisms. Such nanoparticles are biocompatible and can be functionalized easily with different molecules. Nano-sized gold materials were widely used for nucleic acid delivery in animal systems (Martin-Ortigosa et al. 2012a) Recently, Nima et al. (2014) reported the enhanced growth of tobacco cell culture by successful delivery of growth regulator 2,4-D into cells using plasmonically active nanorods based on gold cores and silver shells (Table 8.2).

Table 8.2 Examples of nanomaterials used in plant biotechnological research

Nanomaterials used for delivery	Crop plant	Molecules delivered	References
Gold-plated mesoporous nanoparticle system	Maize	CRE-recombinase protein	Martin-Ortigosa et al. (2014)
Single-walled carbon nanotubes (SWCNTs)	Tobacco protoplasts	DNA	Liu et al. (2009)
Gold silica nanoparticle system (Au-MSN), gold nanorods (NRs)	Onion epidermis tissue	DNA, proteins	Martin-Ortigosa et al. (2012b)
Mesoporous nanoparticle system (MSNS)	Tobacco	DNA and chemicals	Torney et al. (2007)
Gold nanorods (NRs)	Tobacco protoplasts	DNA	Silva et al. (2010)
Gold functionalized silica nanoparticles (Au-MSN)	Onion epidermis tissue	DNA	Martin-Ortigosa et al. (2012a)
Polymer nanoparticles (CPNs)	Tobacco protoplasts	siRNA	Silva et al. (2010)
Nanorods with gold cores and silver shells (AuNR-Ag)	Tobacco callus	Growth regulator 2,4-D	Nima et al. (2014)

8.3.4 Plant Disease Diagnostics and Management

A need for detecting plant disease at an early stage so that tons of food can be protected from the possible outbreak has tempted nanotechnologist to look for a nanosolution for protecting the food and agriculture from bacteria, fungi, and viral agents. Smart field system detects, locates, and reports on pathogens and then applies pesticides and fertilizers as needed prior to the onset of symptoms (Bergeson 2010). Intuitively, nanoparticles can be used as biomarkers or as a rapid diagnostic tool for detection of bacterial, viral, and fungal plant pathogen (Boonham et al. 2008; Yao et al. 2009; Chatuprayoon et al. 2010) in agriculture. Nanoparticle-based sensors might offer improved detection limits in detecting viral pathogen in plants (Baac et al. 2006; Khot et al. 2012). Nanoparticles can either be directly modified to utilize in pathogen detection or used as a diagnostic tool to detect compounds responsible for diseases. Nano-chips are types of microarrays that contain fluorescent oligo-capture probes by which hybridization can be detected (Lopez et al. 2009). These nano-chips are known for their sensitivity and specificity in detection of changes in single nucleotide of viruses and bacteria (Lopez et al. 2009). Yao et al. (2009) used a fluorescence silica nanoparticles in combination with antibody to detect *Xanthomonas axonopodis* pv. *vesicatoria* that causes bacterial spot diseases in solanaceous plants. Singh et al. (2010) used nano-gold-based immune sensors that could detect Karnal bunt (*Tilletia indica*) in wheat using surface plasmon resonance.

Nanoscale materials serve as carriers and provide a broad chemical detection and decision-making ability of self-regulation. These smart systems deliver precise quantities of drugs or nutrients and agrochemicals required. These intelligent systems thus monitor and minimize the use of pesticides and antibiotics (Sharon et al. 2010). Nanotechnologies offer great opportunity to develop new products against pests. Some of the nanoparticles used for controlling plant disease are nanoforms of carbon, silver, silica, and aluminous silicates. Nanoparticles use their optical scattering properties for imaging and diagnostics and their photothermal properties for various types of therapies. The situation was improved by using active molecular targeting with cell-specific molecules (peptides, antibodies) attached to nanoparticles and coupling to cognate receptors at the membranes of specific diseased cells (Lukianova et al. 2011).

Among the different diseases, the viral diseases are the most difficult to control, as one has to stop the spread of the disease by the vectors. But once it starts showing its symptoms, pesticide application would not be of much use. Therefore, detection of exact stage, such as stage of viral DNA replication or the production of initial viral protein, is the key to the success of control of diseases. Nano-based viral diagnostics, including multiplexed diagnostic kit development, have taken momentum in order to detect the exact strain of virus and stage of application of some therapeutic to stop the disease. Detection and utilization of biomarkers that accurately indicate disease stages is also a new area of research. Measuring differential protein production in both healthy and diseased states leads to the identification of the development of several proteins during the infection cycle. These nano-based diagnostic kits not only increase the speed of detection but also increase the power of detection.

Carbon Nanomaterials

Among the various engineered nanomaterials, carbon-based nanomaterials (such as single-walled carbon nanotubes, multi-walled carbon nanotubes, buckyballs, grapheme, etc.) occupy a prominent position in various nanotechnology applications. Increased used and exposure to carbon nanomaterials could cause environmental concerns. Hence, it is extremely important to systematically study the effects that carbon nanomaterials in plants occupy, a major component of the food chain. Carbon nanofibers are used to strengthen natural fibers like those from coconuts (*Cocos nucifera*) and sisal (*Agave sisalana*) and also for making nanoparticles that contain pesticides and control their release (Mishra et al. 2013).

Nanosilver

Nanosilver particles are the most studied and utilized nanoparticle for biological system having a high surface area and fraction of surface atoms. It has strong inhibitory and bacterial effects as well as a broad spectrum of antimicrobial effects that have been used to rid harmful microorganisms and pathogens. Biological synthesis of nanoparticles in sizes ranging from 6 to 38 nm from white radish has been documented. The effectiveness of silver nanoparticles is further enhanced by applying them well before the penetration and colonization of fungal spores within the plant tissues (Duhan et al. 2017). The in vitro and in vivo evaluations of the antifungal action of both silver ions and nanoparticles on *Bipolaris sorokiniana* and *Magnaporthe grisea* showed decreased disease development by phytopathogenic fungi. Spherical-shaped silver nanoparticles in size range of 10–20 nm using culture supernatant of *Serratia* sp. BHU-S4 and their efficacy for the management of spot blotch disease exhibited strong antifungal activity against *Bipolaris sorokiniana*, the spot blotch pathogen of wheat and rose powdery mildew caused by *Sphaerotheca pannosa* var *rosae*. It is a common and widespread disease of both open field and greenhouse causing leaf distortion, leaf curling, early defoliation, and reduced flowering. Using double encapsulated nanosilver eliminates unwanted microorganism in planter soils and hydroponic system. It is being used as foliar spray to top fungi, molds, rot, and several other plant diseases. Moreover, silver is an excellent plant growth stimulator. The efficacy of silver nanoparticles in extending the vase life of gerbera flowers was also studied, and the results showed inhibited microbial growth and reduced vascular blockage which increased the water uptake and maintained the turgidity of gerbera flowers (Nair et al. 2010). Silver in an ionic state exhibits high antimicrobial activity. However, ionic silver is unstable due to its high reactivity and thus gets easily oxidized or reduced into a metal depending on the surrounding media, and it does not continuously exert antimicrobial activity. On the other hand, silica itself has no direct effect on pathogenic microorganisms and has no effect on diseases. Therefore, a new composition of nano-sized silica-silver for control of various plant diseases has been developed (Sharon et al. 2010).

Zinc Oxide

Zinc oxide nanoparticles have shown much better antimicrobial activity than large zinc particles, since the small size is less than 100 nm and high surface-to-volume ratio of nanoparticles allows better interaction with bacteria. Similarly, zinc oxide nanoparticles inhibited the fungal growth of *Botrytis cinerea* by influencing cellular functions, which caused deformation in mycelia mats. In addition, zinc oxide NPs inhibited the growth of conidiophores and conidia of *Penicillium expansum*, which finally led to the death of fungal mats as reported by Abd-elsalam (2013).

Nano-alumino-silicate

Silicon is known to be absorbed into plants to increase disease resistance and stress resistance by promoting physiological activity and growth of plants. Aqueous silicate solution is reported to exhibit exceptional preventive effects on pathogenic microorganisms causing powdery mildew or downy mildew in plants. Additionally, it promotes physiological activity and growth of plants and induces diseases and stress resistance in plants. Nano-alumino-silicate is being used by many leading chemical companies to formulate efficient pesticides at nanoscale. One of such effort is use of alumino-silicate nanotubes with active ingredients to get the advantage of early pick up by insect hairs when used in plant surface. Insects actively groom and consume pesticide-filled nanotubes. They are biologically more active and relatively more environmentally safe pesticides. Silica nanoparticles have also been used to deliver DNA and chemicals to plant, thus creating a powerful new tool for targeted delivery into cells.

Nano-silica-Silver Composite

Silicon (Si) is known to be absorbed into plants and to increase disease resistance and stress resistance (Mao et al. 2001; Brecht et al. 2004). Aqueous silicate solution, used to treat plants, is reported to exhibit excellent preventive effects on pathogenic microorganisms causing powdery mildew or downy mildew in plants thus used for treating diseased plants. Moreover, it promotes physiological activity and growth of plants and induces disease and stress resistance in plants. But since silica has no direct disinfection effects on pathogenic microorganisms in plants, it does not exhibit any effect on established diseases. Further, the effects of silica significantly vary with the physiological environment, and thus, it is not registered as an agricultural chemical. As mentioned above, silver is known as a powerful disinfecting agent. It kills unicellular microorganisms by inactivating enzymes having metabolic functions in the microorganisms by oligodynamic action (Kim et al. 2009).

Titanium Dioxide (TiO_2) Nanoparticles

Khodakovskaya and Lahiani (2014) and Chen et al. (2014) reported that titanium dioxide (TiO_2) is a nontoxic white pigment and a popular photocatalyst used to manufacture pigments. Titanium stimulates production of more carbohydrates, encouraging growth and photosynthetic rates. The application of TiO_2 has been found to show excellent efficacy in maize by reducing the effect of *Curvularia* leaf spot and bacterial leaf blight disease incidence and severity. They also reported that application of TiO_2 significantly reduced the incidence of rice blast and tomato spray mold with a corresponding 20% increase in grain weight due to the growth-promoting effect of TiO_2 nanoparticles (Mahmoodzadeh et al. 2000). Pelaez et al. (2012) reviewed that titanium dioxide has shown photocatalytic activity for the degradation of pesticides. The photocatalytic property of titanium dioxide has application in plant protection because it does form toxic and dangerous compounds, hence possessing great pathogen disinfection efficiency. Scientists are trying to improve the photosynthetic disinfection efficiency of titanium dioxide thin film by doping and other suitable methods. Plants are also the primary choice of researchers for synthesis of titanium dioxide nanoparticles. Spherical-shaped, clustered titanium dioxide nanoparticles with an average size of 32.58 nm from the aqueous leaf extract of *Psidium guajava* have been synthesized (Santhosh kumar et al. 2014). These nanoparticles were tested against bacteria *Aeromonas hydrophila*, *Proteus mirabilis*, *Escherichia coli*, *Staphylococcus aureu*s, and *Pseudomonas aeruginosa*. The maximum zone of inhibition was observed against *Staphylococcus aureus* (25 mm) and *Escherichia coli* (23 mm) when titanium dioxide nanoparticles were used at 20 μg/mL concentration. The synthesized TiO_2 nanoparticles showed enhanced antibacterial activity than the standard antibiotic disk, tetracycline, which reduced the chances for the development of antibiotic resistance of bacterial species. The aqueous extract from plants and titanium dioxide nanoparticles synthesized possessed the best antioxidant activity when compared with ascorbic acid. Synthesis of spherical clusters of quite polydispersed titanium dioxide nanoparticles with a size range from 36 to 68 nm by *Eclipta prostrata* leaf extract has been done successfully as reported by Rajakumar et al. (2012).

There is an urgent need of ultrasensitive rapid diagnostic tool which can detect the molecular defects, either at genomic or biochemical level. Bio-systems are endowed with functional nanometric devices such as enzymes, proteins, and nucleic acids, which detect vital processes in plants. Disease diagnosis is difficult mainly because of the exceptionally low concentrations of biochemical and also due to the presence of very low amounts of detectable virus and many fungal or bacterial infections.

8.3.5 Insect Pest Management

The advances in science and technology in the last decades were made in several areas of pesticides and new ways of application, which include controlled-release formulations (CRF). (Ragaei and Sabry 2014).

Nanopesticides

Nanopesticide is defined as any formulation that intentionally includes elements in the nanometer size range and/or claims novel properties associated with these small size range. Some nanomolecules have already been in the market for several years. Pesticides inside nanoparticles are being developed that can be released slowly or have the release linked to an environmental trigger (Nair et al. 2010; Agrawal and Rathore 2014). Nanopesticides can consist of organic ingredients and/or inorganic ingredients (e.g., metal oxides) in various forms (e.g., particles and micelles). Nanopesticides consist in:

1. Increasing the apparent solubility of poorly soluble active ingredients
2. Releasing the active ingredient in a slow/targeted manner and protecting the active ingredient against premature degradation

Polymers

Applications of polymer in the field of agriculture, highlighting present research trends, impact on food security, and what the future holds are described below.

Functionalized Polymers in Agriculture

Synthetic polymers play an important role in agricultural field as structural materials for creating a climate beneficial to plant growth (e.g., mulches, shelters, or greenhouses, for fumigation and irrigation, in transporting and controlling water distribution). However, the principal requirement of the polymers used in these applications is concerned with their physical properties, such as transmission, stability, and permeability or weatherability and as inert materials rather than as active molecules. During the last few years, the science and technology of reactive functionalized polymers has received considerable interest as one of the most exciting areas of polymer chemistry for the production of improved materials. Functionalized polymers found widespread applications as reactive materials based on the potential advantages of the specific active functional groups and the characteristic properties of the polymeric molecules. Their successful utilizations are quite broad including a variety of fields, such as solid-phase synthesis, biologically active systems, and other various technological uses (Ahmed 1990).

Polymeric Nanobiocides and Herbicides

New techniques have recently emerged for developing controlled-release formulations designed to avoid or reduce the possible side effects accompanying the use of biologically active agents. The purposes of these techniques include to protect the supply of the agent, to allow the automatic release of the agent to the target at controlled rates, and to maintain its concentration within the optimum limits over a specified period of time, thereby producing a great specificity and persistence. There are two different approaches in combining the biological agents with the polymeric materials, either by physical combination (encapsulation or heterogeneous dispersion) to act as a rate controlling device or by chemical combination to act as carrier for the agent (Ahmed 1990). The polymeric biocide has many advantages and its potential benefits include the following: it allows lower amounts than conventional biocides to be used as it releases the required amount of active agent over a long period, the number of applications is reduced because of a long period of activity by a single application, and it eliminates the time and cost of repeated overapplications. The rate of release of active group from the polymer matrix and the consequent duration of the effective action is influenced by chemical characteristics of the active agent's structure; nature of the active agent-polymer bond (such as esters, amides, ureas, urethanes, acetals); the distance of the active agent from the polymer backbone; the necessity of a permanent spacer group to prevent steric hindrance to achieve an enhanced rate of release, the rate of breakdown of the bond between the active material and the polymer by chemical, biological, or environmental agents such as UV, moisture, and microorganisms; chemical nature of the polymer backbone; chemical nature of the groups surrounding the active moieties; dimension and structure of the polymer molecule as governed by the degree of polymerization; monomer's solubility; degree of cross-linking; and the stereochemistry. The main problem with the use of less persistent conventional herbicides that have greater specificity is the use of excess amounts than that actually required to control the herb because they are unstable in an aquatic environment and of the need to compensate the amount wasted by the environmental forces of photodecomposition, leaching, and washing away by rain. They are also highly toxic to farm workers and expensive on multiple applications which are required because of their lower persistence. On the other hand, the applications of large amounts of persistent herbicides are undesirable because of their frequent incorporation into the food chain. In an attempt to reduce the problems encountered in using conventional herbicides, some functionalized polymers containing pesticide moieties as pendant groups have been prepared by free radical polymerization of vinyl monomer type, and their hydrolysis rates were studied under different conditions. As an active pesticide, pentachlorophenol (PCP), a major industrial chemical, represents one of the most widely used biocides in a variety of agrochemical applications, such as herbicide, molluscicide, fungicide, insecticide, algicide, and bactericide. In addition, its hydroxyl group provides a suitable mean for covalent bonding to a variety of polymerizable units. A series of vinyl monomers containing PCP via an ester linkage have been prepared (Sun et al. 1994). These monomers have been homo- and copolymerized with styrene and 4-vinylpridine to induce hydrophobic and hydrophilic nature to the polymers. The rates of release of PCP from the polymers have been studied at four different media (water, pH = 4, pH = 10, and dioxane-water) and all at 30 °C. In addition to PCP, the herbicides of general use that contain functional group for bonding to the polymer matrix have also been used, such as 2,4-dichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid, and 2,4-dinitro-6-methylphenol. The hydrophilic and cross-linking nature of these polymers lead to a faster rate of hydrolytic cleavage of the pendant pesticide. Their rapid deterioration in soil by biodegradation and the subsequent destruction of the polymeric matrix within a short period of time lead to shorter period of effectiveness of the herbicide.

The principle of a dual application of controlled-release herbicide fertilizer has been used (Sun et al. 1994). This principle is based on the use of appropriate polymers as carriers in which the residual products after the degradation of the polymer become beneficial to the plant growth and the soil by acting as fertilizer. For example, herbicide derivatives of bifunctional compounds have been prepared and polymerized under condensation polymerization conditions. The attempt is based on the concept of attaching the herbicides to polymeric hydrogels in order to alter the basic character of sandy soil. In addition to the primary function of these polymers to control the rate of delivery of herbicides, they can also play an important role to increase the water retention by sandy soil through avoiding its rapid leaching. Hence, the use of such dual combination of controlled-release herbicide-water conservation can contribute positively to change the conventional agricultural irrigation especially for sandy soil (Sun et al. 1994). These polymers were developed to improve the physical properties of soil in view of:

1. Increasing their water-holding capacity
2. Increasing water use efficiency
3. Enhancing soil permeability and infiltration rates
4. Reducing irrigation frequency
5. Reducing compaction tendency
6. Stopping erosion and water runoff
7. Increasing plant performance (especially in structureless soils in areas subject to drought)

The presence of water in soil is essential to vegetation. Liquid water ensures the feeding of plants with nutritive elements, which makes it possible for the plants to obtain a better growth rate. It seems to be interesting to exploit the existing water potential by reducing the losses of water and also ensuring better living conditions for vegetation. Taking into account the water-imbibing characteristics of superabsorbent polymer materials, the possibilities of its application in the agricultural field have increasingly been investigated to alleviate certain agricultural problems. SAPs are compounds that absorb water and swell to many times their original size and weight. They are lightly cross-linked networks of hydrophilic polymer chains. The network can swell in water and hold a large amount of water while maintaining the physical dimension structure (Mohammad et al. 2008; Buchholz and

Graham 1997). It was known that commercially used water-absorbent polymeric materials employed are partial neutralization products of cross-linked polyacrylic acids, partial hydrolysis products of starch-acrylonitrile copolymers, and starch-acrylic acid graft copolymers. At present, the material's biodegradability is an important focus of research in this field because of the renewed attention toward environmental protection issues (Lentz 2003). The half-life is in general in the range of 5–7 years, and they degrade into ammonium, carbon dioxide, and water. SAP hydrogels potentially influence soil permeability, density, structure, texture, evaporation, and infiltration rates of water through the soils. Particularly, the hydrogels reduce irrigation frequency and compaction tendency, stop erosion and water runoff, and increase the soil aeration and microbial activity (El-Rehirm abd et al. 2004). The SAP particles may be taken as "miniature water reservoirs" in soil. Water will be removed from these reservoirs upon the root demand through osmotic pressure difference. The hydrogels also act as a controlled-release system by favoring the uptake of some nutrient elements, holding them tightly, and delaying their dissolution. Consequently, the plant can still access some of the fertilizers, resulting in improved growth and performance rates (Liang et al. 2007; Wu et al. 2008). SAPs can also be used as retaining materials in the form of seed additives (to aid in germination and seedling establishment), seed coatings, and root dips and for immobilizing plant growth regulator or protecting agents for controlled release (El-Rehirm abd et al. 2004). The SAP effect on the growth indices of an ornamental plant (*Cupressus arizonica*) under reduced irrigation regimes in the field and on the soil water retention curve in a laboratory was investigated (Abedi-Koupai and Asadkazemi 2006).

All the leading producers of agricultural chemicals, including BASF, Dupont, Monsanto, and Syngenta, are actively conducting research in nanotechnology for use in agriculture and pesticides, and some nanoscale ingredients are already in the market. In the last 10 years, over 3000 patents have been filed for pesticides with nanoscale ingredients. These are mainly reformulations of existing pesticides at the nanoscale. Nanomolecules are generally intended to be more targeted in delivery, to be more toxic, to have greater persistence on leaves, and to allow reduced quantities of chemicals to be used with greater effect (Table 8.3).

8.3.6 Nanomolecules in Recycling Agricultural Waste

Nanomolecules are also used to prevent waste in agriculture, particularly in the cotton industry. When cotton is processed into fabric or garment, some of the cellulose or the fibers are discarded as wasted or used for low-value products such as cotton balls, yarns, and cotton batting. With the use of newly developed solvents and a technique called electrospinning, scientists produce 100 nm diameter fibers that can be used as a fertilizer or pesticide absorbent. These high-performance absorbents allow targeted application at desired time and location. Rice husk, a rice-milling by-product, can be used as a source of renewable energy. When rice

Table 8.3 Polymers used in nanomolecule production

Polymer	Active compound	Nanomolecule	References
Lignin-polyethylene glycol-ethylcellulose	Imidacloprid	Capsule	Flores-Cespedes et al. (2012)
Polyethylene glycol	B-Cyfluthrin	Capsule	Loha et al. (2012)
Chitosan	Etofenprox	Capsule	Hwang et al. (2011)
Polyethylene	Piperonyl butoxide and deltamethrin	Capsule	Frandsen et al. (2010)
Polyethylene glycol	Garlic essential oil	Capsule	Yang et al. (2009)
Poly(acrylic acid)-b-poly(butyl acrylate)-polyvinyl alcohol Polyvinyl pyrrolidone	Bifenthrin	Capsule	Liu et al. (2008)
Acrylic acid-butyl acrylate	Itraconazole	Capsule	Goldshtein et al. (2005)
Carboxymethylcellulose	Carbaryl	Capsule	Isiklan (2004)
Alginate-glutaraldehyde	Neem seed oil	Capsule	Kulkarni et al. (1999)
Alginate-bentonite	Imidacloprid or cyromazine	Clay	Fernandez-Perez et al. (2011)
Polyamide	Pheromones	Fiber	Hellmann et al. (2011)
Starch-based polyethylene	Endosulfan	Film	Jana et al. (2001)
Lignin	Aldicard	Gel	Kok et al. (1999)
Lignin	Amidacloprid or cyromazine	Granules	Fernandez-Perez et al. (2011)
Carboxymethyl chitosan-ricinoleic acid	Azadirachtin	Particles	Feng and Peng (2012)
Chitosan-poly(lactide)	Imidacloprid	Particles	Li et al. (2011)
Polyvinylchloride	Chloropyrifos	Particle	Liu et al. (2002)
Vinyl ethylene and vinyl acetate	Pheromones	Resin	Wright (1997)
Glyceryl ester of fatty acids	Carbaryl	Spheres	Quaglia et al. (2001)
Poly(methyl methacrylate)- poly(ethylene glycol) Polyvinylpyrrolidone	Carbofuran	Suspension	Chin et al. (2011)

Source: Ragaei and Sabry (2014)

husk is burned into thermal energy or biofuel, a large amount of high-quality nanosilica is produced which can be further utilized in making other materials such as glass and concrete. Since there is a continuous source of rice husk, mass production of nanosilica through nanomolecules can alleviate the growing rice husk disposal concern (Mishra et al. 2013).

8.3.7 Nanofertilizers and Nanocomplex

Fertilizers have an axial role in enhancing the food production in developing countries especially after the introduction of high-yielding and fertilizer-responsive crop varieties. In spite of this, it is known that yields of many crops have begun to depress as a result of imbalanced fertilization and decrease in soil organic matter. Moreover, excessive applications of nitrogen and phosphorus fertilizers affect the groundwater. DeRosa et al. (2010) reported that nanofertilizers will combine nanodevices in order to synchronize the release of fertilizer N and P with their uptake by crops, preventing undesirable nutrient losses to soil, water, and air via direct internalization by crops and avoiding the interaction of nutrients with soil, microorganisms, water, and air. Nanostructured formulation might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production and save fertilizer resource. Controlled-release modes having properties of both release rate and release pattern of nutrients for water-soluble fertilizers might be precisely controlled through encapsulation in envelope forms of semipermeable membranes coated by resin-polymer, waxes, and sulfur. Effective duration of nutrient release has desirable property of nanostructured formulation, which can extend effective duration of nutrient supply of fertilizers into soil. Nanostructured formulation can reduce loss rate of fertilizer nutrients into soil by leaching and/or leaking.

The consumption of nitrogen in the form of urea has increased manifold (29%) after the Green Revolution era in India. Increased productivity by applying excess nitrogen is responsible for 80% of the increased in atmospheric N_2O (a greenhouse gas) which causes increased atmospheric temperature and thus contributes to global warming (Park et al. 1940) Chemical fertilizers like urea, diammonium phosphate, and single superphosphate are used in agriculture to meet out the shortage of N, P, and K in the soil. But most part of these fertilizers are lost off or volatilized. It is estimated that about 40–70% nitrogen, 80–90% phosphorus, and 50–70% potassium of the applied fertilizers are lost to the environment and can't be absorbed by plants causing exchequer loss to the nation and environmental pollution as well. Moaveni and Kheiri (2011) reported that nanofertilizer technology is very innovative; however, only very scantly reported literatures are available in the scientific journals. Substituting nanofertilizers for traditional methods of fertilizer application is a way to release nutrients into the soil gradually and in a controlled way, thus preventing purification and pollution of water resources. DeRosa et al. (2010) reported that in nanofertilizers, nutrients can be encapsulated by nanomaterials, with a thin protective coating, or delivered as emulsions or nanoparticles. Nanotech materials are being developed for slow release and efficient dosages of fertilizers for plant and have the potential to increase the efficiency of nutrient uptake (Singh 2012; Sekhon 2014). An enhanced production has been observed by foliar application of nanoparticles as fertilizer. A variety of nanomaterials, mostly metal-based nanomaterials and carbon-based nanomaterials, have been exploited for their absorption, translocation, accumulation, and productivity, affecting on growth and development in an array of crop plants (Nair et al. 2010; Rico et al. 2011).

Nanosizing, in theory, should make fertilizer nutrients more available to nanoscale plant pores and therefore result in efficient nutrient use (Suppan 2013). “Intelligent nanofertilizer” has been proposed with nano-sized biosensors suspended in a biopolymer that coats micron-sized fertilizer particles. Nanomaterials used in recommended doses may sometimes fail to exert the desired effects due to concentration of these materials which is much below the minimum effective concentration required of the chemicals that has to reach the target site of crops due to obstacles such as leaching of chemicals, degradation by photolysis or microbes, and hydrolysis. Hence, repetitive application is indispensable to have an effective control consequently, which might cause some unfavorable effects such as soil and water pollution. Nanoencapsulated agrochemicals should be designed in such a way that they possess all indispensable properties such as effective concentration (with high solubility, stability, and effectiveness), time-controlled release in response to certain stimuli, enhanced targeted activity, and less ecotoxicity with harmless and effortless mode of delivery, thus avoiding repetitive application (Nair et al. 2010). Slow-release fertilizers are excellent alternatives to soluble fertilizers as nutrients are released at a slower rate throughout the crop growth; plants are able to take up most of the nutrients without waste by leaching. Slow release of nutrients in the environments could be achieved by using zeolites.

Zeolites

Zeolites are a group of naturally occurring minerals having a honeycomb-like-layered crystal structure, and their network of interconnected tunnels and cages can be laden with nitrogen and potassium along with other slowly dissolving ingredients containing phosphorous, calcium, and a complete suite of minor and trace nutrients. Fertilizer particles can be coated with nano-membranes that facilitate slow and steady release of nutrients, e.g., patented nanocomposite containing N, P, K, micronutrients, mannose, and amino acids that enhanced the uptake and utilization of nutrients by grain crops has been reported (Chinnamuthu and Boopathi 2009).

Carbon Nanotubes

Carbon nanotubes are allotropes of carbon with cylindrical shape and can be utilized as vehicle to deliver desired molecules, either nutrient or biocides, into the seeds during germination. Similarly, triazophos can also be effectively protected from hydrolysis in acidic and neutral media by including it in a nanoemulsion (Gutiérrez et al. 2011). Now a days these became attractive electronic materials to date and their replication in future electric circuits and biosensing chips (Yan et al. 2011). It acts as vehicle to deliver desired molecules into the seeds during germination that can protect them from the diseases. Since it is growth promoting, it will not have any toxic or inhibiting or adverse effect on the plant.

Copper and Silica

A combination of titanium dioxide, aluminum, and silica was reported to be effective in controlling downy and powdery mildew of grapes by Bowen et al. (1992), possibly through direct action on the hyphae, interference with recognition of plant surface, and stimulation of plant physiological defenses. Nanosilica has been successfully employed to control a range of agricultural insect/pest. Such nanoparticles get absorbed into cuticular lipids (used by insects to prevent death from desiccation) by physisorption and cause insect death by physical means when applied on leaves and stem surfaces (Ulriches et al. 2005). Antifungal activities of polymer-based copper nanocomposites against pathogenic fungi (Cioffi et al. 2004) and silica-silver nanoparticles against *Botrytis cinerea*, *Rhizoctonia solani*, *Colletotrichum gloeosporioides* (Park et al. 2006), *Bipolaris sorokiniana*, and *Magnaporthe grisea* (Jo et al. 2009) have been reported. Copper nanoparticles in soda lime glass powder showed efficient antimicrobial activity against gram-positive and gram-negative bacteria and fungi (Esteban-Tejeda et al. 2009).

Tetramethylammonium Hydroxide

Magnetic nanoparticles coated with tetramethylammonium hydroxide led to an increase in chlorophyll-a level in maize (1994). Use of iron oxide in pumpkin was also observed to increase root elongation that was attributed to the iron dissolution.

8.3.8 Nanotechnologies for Water Quality and Availability

Currently, provision of clean and abundant freshwater is one of the most important challenges faced by the world for human use and industrial applications such as agriculture. According to a survey, more than one billion people in the world are deprived of clean water and the situation is getting worse. In the near future, it has been estimated that the average water supply per person will drop by a factor of one third, which will result in the avoidable premature death of millions of people (Cross et al. 2009). A large amount of freshwater is required in agriculture, but in turn, it contributes to groundwater pollution through the use of pesticides, fertilizers, and other agricultural chemicals. To combat this problem, novel, sustainable, and cost-effective technologies will be required for the treatment of this large amount of wastewater produced. During the treatment of wastewater, critical issues like water quality and quantity, treatment and reuse, safety due to chemical and biological hazards, and monitoring and sensors should be considered. Research and development in nanotechnology has enabled us to find novel and economically feasible solutions for remediation and purification of this wastewater. Accessible water resources are mostly contaminated with waterborne pathogenic microorganisms like cryptosporidium, coliform bacteria, virus, etc., various salts and metals (Cu, Pb, As, etc.), and runoff agricultural chemicals.

Nangmenyi and Economy (2009) reported physicochemical microbial disinfection systems like chlorine dioxide, ozone, and ultraviolet are being commonly used in developed countries, but most of the developing countries are lacking these systems due to the requirement of large infrastructure which makes them costly. The need of the hour is to search and develop alternative cost-effective technologies. Nanotechnology-based oligodynamic metallic particles have the ability to serve this function. Among these nanomaterials, silver is the most promising one as it is both bactericidal and viricidal due to the production of reactive oxygen species that cleaves DNA and can be utilized for a wide range of applications. Other properties include low toxicity, ease of use, its charge capacity, high surface-to-volume ratios, crystallographic structure, and adaptability to various substrates.

Hoek and Ghosh (2009) emphasized on desalination of seawater which will be become a major source of freshwater due to limited resources of freshwater for agriculture and domestic purposes. Conventional desalination technologies like reverse osmosis membranes are being used, but these are costly due to the large amount of energy required. Nanotechnology has played a very important role in developing a number of low-energy alternatives, among which three are most promising: (i) protein-polymer biomimetic membranes, (ii) aligned carbon nanotube membranes, and (iii) thin-film nanocomposite membranes. These technologies have shown up to 1000 times better desalination efficiencies than reverse osmosis, as these have high water permeability due to the presence of carbon nanotube membranes in their structure. Some of these membranes are involved in the integration of other processes like disinfection, deodorizing, de-fouling, and self-cleaning. Some of these technologies may be introduced in the marketplace in the near future, but scale-up fabrication, practical desalination effectiveness, and long-term stability are the most critical challenges to be considered before their successful commercialization.

8.3.9 Phytochemicals and Essential Oils

Phytochemicals such as secondary metabolites and essential oils proved to have eco-friendly biological activity, but they face problems of stability and cost-effectiveness. As observed by Ghormade et al. (2010), an essential oil from *Artemisia arborescens* faced the problem of instability during pesticide activity against *Aphis gossypii* (citrus fruit pest), adult and young *Bemisia tabaci*, and *Lymantria dispar* (cork plant pest). Incorporation of *A. arborescens* essential oil into solid lipid nanoparticles (200–294 nm) reduced the rapid evaporation of essential oil, in comparison to the reference emulsions. Similarly, the essential oil from garlic when loaded on polymer nanoparticles (240 nm) coated with polyethylene glycol to evaluate their insecticidal activity against adult *Tribolium castaneum* showed more than 80% efficacy even after 5 months, due to the controlled slow release of the active components, in comparison to free garlic essential oil (11%). This indicated the feasibility of polyethylene glycol-coated nanoparticles loaded with garlic essential oil for control of storage pests (Ghormade et al. 2010).

8.3.10 Nanotech Delivery Systems for Pests and Nutrients

Nano-based smart delivery systems and nanosensors could help in the efficient use of natural resources like water, nutrients, and chemicals through precision farming. Through the use of nanomaterials and global positioning systems with satellite imaging of fields, farm managers could remotely detect crop pests or evidence of stress such as drought. Once pest or drought is detected, there would be automatic adjustment of pesticide applications or irrigation levels. Nanosensors dispersed in the field can also detect the presence of plant viruses and the level of soil nutrients. Nanoencapsulated slow-release fertilizers have also become a trend to save fertilizer consumption and to minimize environmental pollution.

8.3.11 Nanosensors/Nanobiosensors in Agri-food Production

Crop growth and field conditions like moisture level, soil fertility, temperature, crop nutrient status, insects, plant diseases, weeds, etc. can be monitored through advancement in nanotechnology. This real-time monitoring is done by employing networks of wireless nanosensors across cultivated fields, providing essential data for agronomic intelligence processes like optimal time of planting and harvesting the crops. It is also helpful for monitoring the time and level of water, fertilizers, pesticides, herbicides, and other treatments. These processes are needed to be administered given specific plant physiology, pathology, and environmental conditions and ultimately reduce the resource inputs and maximize yield (Scott and Chen 2003). Nanobiosensors can be effectively used for sensing a wide variety of fertilizers, herbicides, insecticides, pathogens, moisture, and soil pH, and their control can support sustainable agriculture for enhancing crop productivity (Rai et al. 2012). The development of sensor-/biosensor-based specific interaction makes atomic force spectrometry more effective in detecting enzyme-inhibiting herbicides. Noble metal (palladium, platinum, and gold)/DNA/single-walled carbon nanotube (SWCNT) hybrid nanostructure-based gas sensor arrays were fabricated by means of inkjet printing of metal ion-chelated DNA/SWCNTs on microfabricated electrodes followed by electrodeless deposition to reduce metal ions to metal. DNA serve as a dispersing agent to effectively solubilize pristine SWCNTs in water and as metal ion-chelating centers for the formation of nanoparticles. Nanobarcodes and nanoprocessing could also be used to monitor the quality of agricultural product. Scientists at Cornell University used the concept of grocery barcodes for cheap, efficient, rapid, and easy decoding and detection of diseases. They produced microscopic probes or nanobarcodes that could tag multiple pathogens in a farm which can easily be detected using any fluorescent-based equipment. This ongoing project generally aims to develop a portable on-site detector which can be used by non-trained individuals. Scientists and engineers are working from dawn to dusk in developing the strategies which can increase the water use efficiency in agricultural productions, e.g., drip irrigation. This has moved precision agriculture to a much higher level of control in water usage, ultimately toward the conservation of water. More precise water delivery systems are likely to be developed in the near future. These factors critical for their development include water storage, in situ water-holding capacity, water distribution near roots, water absorption efficiency of plants, encapsulated water released on demand, and interaction with field intelligence through distributed nanosensor systems (Cross et al. 2009).

8.3.12 Plant Hormones

Through nanomolecule, researchers are able to study plant's regulation of hormones such as auxin, which is responsible for root growth and seedling establishment. Scientists at Purdue University developed a nanosensor that reacts with auxin. This interaction generates an electrical signal which can be a basis for measuring auxin concentration at a particular point. The nanosensor oscillates, taking auxin concentration readings at various points of the root. This is a breakthrough in auxin research because it helps scientists understand how plant roots adapt to their environment, especially to marginal soils (Mishra et al. 2013).

8.3.13 Quality of Agricultural Food Products

Nanotechnology also has applications in the agri-food sector. Many vitamins and their precursors, such as carotenoids, are insoluble in water. However, when formulated as nanoparticles, these substances can easily be mixed with cold water, and their bioavailability in the human body also increases. Many lemonades and fruit juices contain these specially formulated additives, which often also provide an attractive color. The world market potential of such micron-sized compounds is estimated to be $1 billion. In the near future bio- and gas sensors could gain importance. These sensors could be integrated into packaging materials to monitor the freshness of the food. Bio-selective surfaces are the new innovation of nanoscience technology with a principle that surfaces are the environment and location on which most chemical and biological interactions occur. A bio-selective surface has either an enhanced or reduced ability to bind or hold specific organisms or molecules.

8.3.14 Bioengineering

A huge amount of agricultural products and foods are wasted starting from the harvest at the field to their transportation, storage, and further processing. This important rate-limiting factor can possibly be addressed by enhancing the capacity of the country in relation to high-throughput experimental technologies. Nanotechnology is a part of any nation's future. Research on nanomaterials has extremely high potential to benefit society through applications in agriculture and food systems. As in the case of almost every nonconventional technology, e.g., genetic engineering, some fear that nanotechnology can give people too much control. We believe that this control can be wisely used and that the huge contributions that nanotechnology can make very strong arguments in favor of using this revolutionary science to its fullest potential. Food and agriculture technology should take advantage of the powerful tools of nanotechnology, for the benefit of humankind. Application of nanomolecule-based products in agricultural field is shown in Table 8.4.

8.4 Conclusion

New tools using nanomaterials are underway which will be equipped with nanodevices. Use of nanomaterials could permit rapid advances in agricultural research which will produce large amount of fruits unaffected by season and growing period. The potential use and benefits of nanoparticle-based technology are enormous. Productivity enhancement by using nanoparticle-driven precision

Table 8.4 Relevant application of agricultural nanotechnology and examples of successful applications

Application	Nanomolecules	Examples	References
Crop production			
Plant protection product	Nanocapsules, nanoparticles, nanoemulsions, and viral capsids as smart delivery systems of active ingredients for biotic stress management	Neem oil (*Azadirachta indica*), monoemulsion as larvicidal agent (VIT University, IN)	CH Anjali, Y Sharma, A Mukherjee, N Chandrasekaran (2012) Pest Manage Sci 68: 158—163
Fertilizers	Nanocapsules, nanoparticles, and viral capsids for the enhancement of nutrient absorption by plants and the delivery of nutrients to specific sites	Macronutrient fertilizers coated with zinc oxide nanoparticles (University of Adelaide, AU; CSIRO Land and Water, AU; Kansas State University, USA)	N Milani, et al. (2012) J Agric Food Chem. 60: 3991–3998
Soil improvement			
Water/liquid retention product	Nanomaterials, e.g., zeolites and nanoclays, for water or liquid agrochemical retention in the soil for their slow release to the plants	Soil-enhancer product, based on a nanoclay component, for water retention and release (Geohumus-Frankfurt, DE)	http://www.geohumus.com/us/products.html
Water purification			
Water purification and pollutant remediation	Nanomaterials, e.g., nanoclays, filtering and binding to a variety of toxic substances, including pesticides, to be removed from the environment	Filters coated with TiO_2 nanoparticles for the photocatalytic degradation of agrochemicals in contaminated waters (University of Ulster, UK)	TA McMurray, PSM Dunlop, JA Byrne (2006) J Photochem Photobiol A-Chem 182: 43–51
Diagnostic			
Nanosensors and diagnostic devices	Nanomaterials and nanostructures (e.g., electrochemically active carbon nanotubes, nanofibers, and fullerenes) that are highly sensitive biochemical sensors to closely monitor environmental conditions, plant health, and growth	Pesticide detection with a liposome-based nanobiosensor (University of Crete, GR)	V Vamvakaki, NA Chaniotakis (2007) Biosens Bioelectronics 22:2848–2853.
Plant breeding			
Plant genetic modification	Nanoparticles carrying DNA or RNA to be delivered to plant cells for their genetic	Mesoporous silica nanoparticles transporting DNA to transform plant cells	F Torney, BG Trewyn, VSY Lin, K Wang (2007) Nat

(continued)

Table 8.4 (continued)

Application	Nanomolecules	Examples	References
	transformation or to trigger defense responses, activated by pathogens	(Iowa State University, USA)	Nanotechnol 2: 295–300
Nanomaterials from plant			
Nanoparticles from plants	Production of nanomaterials through the use of engineered plants or microbes and through the processing of waste agricultural products	Nanofibers from wheat straw and soy hulls for bio-nanocomposite production (Canadian Universities and Ontario Ministry of Agriculture, Food and Rural Affairs, CA)	A Alemdar, M Sain (2008) Bioresour Technol 99: 1664–1671

Parisi et al. (2015)

farming and maximization of output and minimization of inputs through better monitoring and targeted action is desirable. Use of nanomaterials in agricultural research enables plants to use water, pesticides, and fertilizers more efficiently. Anticipated nanoparticle-based application includes nanosensor/nanobiosensor for detecting pathogen and for soil quality for plant health monitoring. Experts envision numerous nanoparticle agro-formulations with higher bioavailability and efficacy and better selectivity in the near future. Multidisciplinary approaches could potentially improve food production, incorporating new emerging technologies and disciplines such as chemical biology integrated with nanotechnologies to tackle existing bottlenecks that currently limit further developments.

References

Abd El-Rehirm HA, Hegazy ESA, Abd El-Mohdy HL (2004) Radiation synthesis of hydrogels to enhance sandy soils water retention and increase performance. J Appl Polym Sci 93:1360–1371

Abd-elsalam KA (2013) Fungal genomics & biology nanoplatforms for plant pathogenic fungi management. Fungal Genom Biol 2:107

Abedi-Koupai J, Asadkazemi J (2006) Effects of a hydrophilic polymer on the field performance of an ornamental plant (*Cupressus arizonica*) under reduced irrigation regimes. Iran Polym J 15:715–725

Agrawal S, Rathore P (2014) Nanotechnology pros and cons to agriculture: a review. Int J Curr Microbiol Appl Sci 3:43–55

Ahmed A (1990) Applications of functionalized polymers in agriculture. J Islam Acad Sci 3 (1):49–61

Baac H, Hajós JP, Lee J, Kim D, Kim SJ, Shuler ML (2006) Antibody-based surface plasmon resonance detection of intact viral pathogen. Biotechnol Bioeng 94(4):815–819

Bergeson LL (2010) Nanosilver: US EPA's pesticide office considers how best to proceed. Environ Qual Manag 19(3):79–85

Bernhardt ES, Colman BP, Hochella MF, Cardinale BJ, Nisbet RM, Richardson CJ, Yin L, Boonham N, Glover R, Tomlinson J, Mumford R (2008) Exploiting generic platform technologies for the detection and identification of plant pathogens. Eur J Plant Pathol 121:355–363

Bouwmeester H, Dekkers S, Noordam MY, Hagens WI, Bulder AS, de Heer C, ten Voorde SECGS, Wijnhoven WP, Marvin HJP, Sips AJAM (2009) Review of health safety aspects of nanotechnologies in food production. Regul Toxicol Pharmacol 53:52–62

Boonham N, Glover R, Tomlinson J, Mumford R (2008) Exploiting generic platform technologies for the detection and identification of plant pathogens. Eur J Plant Pathol 121(3):355–363

Bowen P, Menzies J, Ehret D, Samuel L, Glass ADM (1992) Soluble silicon sprays inhibit powdery development in grape leaves. J Am Soc Hortic Sci 117:906–912

Bradley EL, Castle L, Chaudhry Q (2011) Applications of nanomaterials in food packaging with a consideration of opportunities for developing countries. Trends Food Sci Technol 22:604–610

Brecht MO, Datnoff LE, Kucharek TA, Nagata RT (2004) Influence of silicon and chlorothalonil on the suppression of gray leaf spot and increase plant growth in St. Augustine grass. Plant Dis 88:338–344

Buchholz and Grahm (1997): https://www.wiley.com/en-us/Modern+Superabsorbent+Polymer+Technology-p-9780471194118

Canas JE, Long M, Nations S, Vadan R, Dai L, Luo M, Ambikapathi R, Lee EH, Olszyk D (2008) Effects of functionalized and nonfunctionalized single-walled carbon nanotubes on root elongation of select crop species. Environ Toxicol Chem 27:1922–1931

Chartuprayoon N, Rheem Y, Chen W, Myung NV (2010) Detection of plant pathogen using LPNE grown single conducting polymer nanoribbon. Abstract #2278, 218th ECS meeting

Chen K, Arora R (2013) Priming memory invokes seed stress-tolerance. Environ Exp Bot 94:33–45

Chen H, Seiber JN, Hotze M (2014) ACS select on nanotechnology in food and agriculture: a perspective on implications and applications. J Agric Food Chem 62:1209–1212

Chin et al. (2011): https://pubs.acs.org/doi/10.1021/ie2001007

Chinnamuthu CR, Boopathi PM (2009) Nanotechnology and agroecosystem. Madras Agric J 96:17–31

Cioffi N, Torsi L, Ditaranto N (2004) Antifungal activity of polymer-based copper nanocomposite coatings. Appl Phys Lett 85(12):2417–2419

Cross KM, Lu Y, Zheng T, Zhan J, McPherson G, John V (2009) Chapter 24: Water decontamination using iron and iron oxide nanoparticles. In: Savage N, Diallo M, Duncan J, Street A, Sustich R (eds) Nanotechnology applications for clean water. William Andrew Inc, Norwich, p 347

De la Rosa G, Lopez-Moreno ML, de Haro D, Botez CE, Peralta-Videa JR, Gardea-Torresdey JL (2013) Effects of ZnO nanoparticles in alfalfa, tomato, and cucumber at the germination stage: root development and X-ray absorption spectroscopy studies. Pure Appl Chem 85:2161

DeRosa MC, Monreal C, Schnitzer M, Walsh R, Sultan Y (2010) Nanotechnology in fertilizers. Nat Nanotechnol 5(2):91

Duhan JS, Kumar R, Kumar N, Kaur P, Nehra K, Duhan S (2017) Nanotechnology the new perspective in precision agriculture. Biotechnol Reports 15:11–23

El-Temsah YS, Joner EJ (2010) Impact of Fe and Ag nanoparticles on seed germination and differences in bioavailability during exposure in aqueous suspension and soil. Environ Toxicol 27:42

Emamifar A, Kadivar M, Shahedi M, Soleimanian-Zad S (2010) Evaluation of nanocomposite packaging containing Ag and ZnO on shelf life of fresh orange juice. Innov Food Sci Emerg Technol 11:742–748

Esteban-Tejeda L, Malpartida F, Esteban-Cubillo A, Pecharromán C, Moya JS (2009) Antibacterial and antifungal activity of a soda-lime glass containing copper nanoparticles. Nanotechnology 20 (50):505–701

Feng BH and Peng LF (2012) Synthesis and characterization of carboxymethyl chitosan carrying ricinoleic functions as an emulsifier for azadirachtin. Carboh Polym 88:576–582

Fernandez-Penez M, Garrido-Herrara FJ, Gonzalez Prades E (2011) Alginate and lignin based formulation to control pesticides leaching in a calcareous soil. J Hazard Mater 190 (1–3):794–801

Flores-Cespedes F, Figueredo-Flores CI, Daza-Fernandez I, Vidal-Pena F, Villafranca Sanchez M, Fernandez-Perez M (2012) Preparation and characterization of Imidacloprid Lignin-Polyethylene glycol matrices coated with Ethylcellulose. J Agric Food Chem 60:1042–1051

Frandsen MV, Pedersen MS, Zellweger M, Gouin S, Roorda SD, Phan TQC (2010) Piperonyl butoxide and deltamethrin containing insecticidal polymer matrix comprising HDPE and LDPE. Patent number WO 2010015256 A2 20100211

Ghormade V, Deshpande MV, Paknikar KM (2010) Perspectives for nanobiotechnology enabled protection and nutrition of plants. Biotechnol Adv 29:792–803

Goldshtein R, Jaffe I, Tulbovich B (2005) Hydrophilic dispersions of nanoparticles of inclusion complexes of amorphous compounds. Patent number US 20050249786A120051110

Gutiérrez FJ, Mussons ML, Gatón P, Rojo R (2011) Nanotechnology and food industry. Scientific, health and social aspects of the food industry. In Tech, Croatia Book Chapter

Hellmann C, Greiner A, Wendorff JH (2011) Design of pheromone releasing nanofibers for plant protection. Pol Adv Technol 22:407–413

Hoek EMV, Ghosh AK (2009) Chapter 4: Nanotechnology-based membranes for water purification. In: Savage N, Diallo M, Duncan J, Street A, Sustich R (eds) Nanotechnology applications for clean water. William Andrew Inc, Norwich, p 47

Horii A, McCue P, Shetty K (2007) Seed vigour studies in corn, soybean and tomato in response to fish protein hydrolysates and consequences on phenolic- linked responses. Bioresour Technol 11:2170–2177

Hussain S et al (2015) Benefits of rice seed priming are offset permanently by prolonged storage and the storage conditions. Sci Rep 5:8101

Hwang IC, Kim TH, Bang SH, Kim KS, Kwon HR, Seo MJ, Youn YN, Park HJ, Yasunaga-Aoki C, Yu YM (2011) Insecticidal effect of controlled release formulations of etofenprox based on nano-bio technique. J Fac Agric Kyushu Univ 56:33–40

Ibrahim EA (2016) Seed priming to alleviate salinity stress in germinating seeds. J Plant Physiol 192:38–46

Isiklan N (2004) Controlled release of insecticide carbaryl from crosslinked carboxymethyl cellulose beads. Fre Environ Bull 13:537–544

Jana T, Roy BC, Maiti S (2001) Biodegradable film 6. Modification of the film for control release of insecticides. Eur Pol J 37:861–864

Jo YK, Kim BH, Jung G (2009) Antifungal activity of silver ions and nano-particles on phytopathogenic fungi. Plant Dis 93(10):1037–1043

Khodakovskaya MV, Lahiani MH (2014) Nanoparticles and plants: from toxicity to activation of growth. In: Sahu SC, Casciano DA (eds) Handbook of Nanotoxicology, nanomedicine and stem cell use in toxicology. Wiley, New York, pp 121–130

Khodakovskaya M, Dervishi E, Mahmood M, Xu Y, Li Z, Watanabe F, Biris AS (2009) Carbon nanotubes are able to penetrate plant seed coat and dramatically affect seed germination and plant growth. ACS Nano 3:3221–3227

Khodakovskaya MV, de Silva K, Biris AS, Dervishi E, Villagarcia H (2012) Carbon nanotubes induce growth enhancement of tobacco cells. ACS Nano 6:2128

Khot Lav R, Sankaran S, Mari MJ, Ehsanireza SEW (2012) Application of nanomaterials in agricultural production and crop protection. A review. Crop Prot 35:64–70

Kim SW, Kim KS, Lamsal K, Kim YJ, Kim SB, Jung M, Sim SJ, Kim HS, Chang SJ, Kim JK, Lee YS (2009) An in vitro study of the antifungal effect of silver nanoparticles on oak wilt pathogen *Raffaelea* sp. J Microbiol Biotechnol 19:760–764

Kok FN, Wilkins RM, Cain RB, Arica MY, Alaeddinoglu G, Hasirci V (1999) Controlled release of aldicarb from lignin loaded ionotropic hydrogel microspheres. J Microencapsul 16:613–623

Kulkarni AR, Soppimath KS, Aminabhavi TM, Dave AM, Mehta MH (1999) Application of sodium alginate beads crosslinked with glutaraldehyde for controlled release of pesticide. Polym News 2:285–286

Larue C, Veronesi G, Flank AM, Surble S, Nathalie HB, Carrière M (2012) Comparative uptake and impact of TiO nanoparticles in wheat and rapeseed. J Toxic Environ Health Part A 75 (13–15):722–734

Lee WM, An YJ, Yoon H, Kweon HS (2008) Toxicity and bioavailability of copper nanoparticles to the terrestrial plants Mungbean (*Phaseolus radiatus*) and wheat (*Triticum aestivum*): pant agar test for waterinsoluble nanoparticles. Environ Toxic Chem 27(9):1915

Lee J, Mahendra S, Alvarez PJJ (2010) Nanomaterials in the construction industry: a review of their applications and environmental health and safety considerations. ACS Nano 4(7):3580–3590

Lentz RD (2003) Inhibiting water infiltration with PAM and surfactants: applications for irrigated agriculture. J Soil Water Conserv 58:290–300

Li M, Huang Q, Wu Y (2011) A novel chitosan-poly (Lactide) copolymer and its submicron particles as imidacloprid carriers. Pest Manag Sci 67:831–836

Liang M, Zhan R, Liu Z, Niu A (2007) Preparation of superabsorbent slow release nitrogen fertilizer by inverse suspension polymerization. Polym Int 56:729–737

Lin D, Xing B (2007) Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. Environ Pollut 150:243–250

Liu Y, Laks P, Heiden P (2002) Controlled release of biocides in solid wood. ii.efficacy against *Trametes versicolor* and *Gloeophyllum trabeum* wood decay fungi. J Appl Polym Sci 86:608–614

Liu Y, Tong Z, Prud'homme RK (2008) Stabilized polymeric nanoparticles for controlled and Agricultural efficient release of bifenthrin. Pest Manag Sci 64:808–812

Liu Q, Chen B, Wang Q, Shi X, Xiao Z, Lin J, Fang X (2009) Carbonnanotubes as moleculer atranspoters for walled plant cells. Nano Lett 9:1007–1019

Loha KM, Shakil NA, Kumar J, Singh MK, Srivastava C (2012) Bio-efficacy evaluation of nanoformulations of cyfluthrin against *Callosobruchus maculatus* (Coleoptera: Bruchidae). J Environ Sci Health Part B 47:687–691

López MM, Llop P, Olmos A, Marco-Noales E, Cambra M, Bertolini E (2009) Are molecular tools solving the challenges posed by detection of plant pathogenic bacteria and viruses? Curr Issues Mol Biol 11:13–46

Lopez-Moreno ML, De La Rosa G, Hernandez-Viezcas JA, Peralta-Videa JR, Gardea-Torresdey JL (2010) X-ray absorption spectroscopy (XAS) corroboration of the uptake and storage of CeO_2 nanoparticles and assessment of their differential toxicity in four edible plant species. J Agric Food Chem 58:3689

Lu C, Zhang C, Wen J, Wu G, Tao M (2002) Research on effect of nanometer materials on germination and growth enhancement of *Glycine max* and its mechanism. Soybean Sci 21:168

Lukianova-Hleb EY, Oginsky AO, Shenefelt DL, Drezek RA, Hafner JH (2011) Rainbow Plasmonic Nanobubbles: synergistic activation of gold nanoparticle clusters. J Nanomed Nanotechnol 2:104

Mahakham W, Sarmah AK, Maensiri S, Theerakulpisut P (2017) Nanopriming technology for enhancing germination and starch metabolism of aged rice seeds using phytosynthesized silver nanoparticles. Sci Rep 7:8263. https://doi.org/10.1038/s41598-017-08669-5

Mahmoodzadeh H, Nabavi M, Kashefi H (2000) Effect of nanoscale titanium dioxide particles on the germination and growth of canola *Brassica napus*. J Ornam Hortic Plants 3:25–32

Mao HQ, Roy K, Troung-Le VL, Janes KA, Lin KY, Wang Y, August JT, Leong KW (2001) Chitosan-DNA nanoparticles as gene carriers: synthesis, characterization and transfection efficiency. J Control Release 70:399–421

Martin-Ortigosa S, Valenstein JS, Lin VS, Trewyn BG, Wang K (2012a) Gold functionalized mesoporous silica nanoparticle mediated protein and DNA Codelivery to plant cells via the biolistic method. Adv Funct Mater 22(17):3576–3582

Martin-Ortigosa S, Valenstein JS, Sun W, Moeller L, Fang N, Trewyn BG, Lin VS, Wang K (2012b) Parameters affecting the efficient delivery of mesoporous silica nanoparticle materials and gold Nanorods into plant tissues by the biolistic method. Small 8(3):413–422

Martin-Ortigosa S, Peterson DJ, Valenstein JS, Lin VS, Trewyn BG, Lyznok LA, Wang K (2014) Mesoporous silica nanoparticle mediated intraceller cre protein delivery for maize genome editing via lox P site excition. Plant Physiol 164(537):547

Miralles P, Johnson E, Church TL, Harris AT (2012) Multiwalled carbon nanotubes in alfalfa and wheat: toxicology and uptake. J Rl Soc Interface 9:3514

Mirzajani F, Askari H, Hamzelou S, Farzaneh M, Ghassempour A (2013) Effect of silver nanoparticles on Oryza sativa L. and its rhizosphere bacteria. Ecotoxicol Environ Saf 88:48

Mishra VK, Dwivedi DK, Mishra UK (2013) Emerging consequence of nanotechnology in agriculture: an outline. Trends Biosci 6(5):503–506

Moaveni P, Kheiri T (2011) TiO_2 nano particles affected on maize (*Zea mays* L). In: 2nd international conference on agricultural and animal science, November 25–27, Maldives. IACSIT Press, Singapore, pp 160–163

Mondal A, Basu R, Das S, Nandy P (2011) Beneficial role of carbon nanotubes on mustard plant growth: an agricultural prospect. J Nanopart Res 13:4519

Mohammad J, Mehr Z, Kabiri K (2008) Super absorbent polymer materials. A Review, Iranian Polym J 17(6):451–477

Morla S, Ramachandra Rao CSV, Chakrapani R (2011) Factors affecting seed germination and seedling growth of tomato plants cultured in vitro conditions. J Chem Biol Phys Sci B 1:328

Nair R, Varghese SH, Nair BG, Maekawa T, Yoshida Y (2010) Nanoparticulate material delivery to plants. Plant Sci 179:154–163

Nangmenyi G, Economy J (2009) Chapter 1: Nonmetallic particles for oligodynamic microbial disinfection. In: Savage N, Diallo M, Duncan J, Street A, Sustich R (eds) Nanotechnology applications for clean water. William Andrew Inc, Norwich, p 3

Nima AZ, Lahiani MH, Watanabe F, Xu Y, Khodakovskaya MV, Biris AS (2014) Plasmonically active nanorods for delivery of bio-active agents and high-sensitivity SERS detection in planta. RSC Adv 4(110):64985–64993

Ochatt S (2013) Plant cell electrophysiology: applications in growth enhancement, somatic hybridisation and gene transfer. Biotechnol Adv 31(8):1237–1246

Parisi C, Vigani M, Rodriguez-cerezo E (2015) Agricultural nanotechnologies: what are the current possibilities. NanoToday 10:124–127

Park S, Croteau P, Boering KA, Etheridge DM, Ferretti DP, Fraser J, Kim KR, Krumme PB, Langenfelds RLTDV, Ommen LP, Steele CM (1940) Trudinger, trends and seasonal cycles in the isotopic composition of nitrous oxide since. Nat Geosci 5:261–265

Park HJ, Kim SH, Kim HJ, Choi SH (2006) A new composition of nanosized silica-silver for control of various plant diseases. Plant Pathol J 22(3):295–302

Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P, Kontos AG, Dunlop PS, Hamilton JW, Byrne JA, O'Shea K (2012) A review on the visible light active titanium dioxide photocatalysts for environmental applications. Appl Catal B Environ 125:331–349

Prasad TNVKV, Sudhakar P, Sreenivasulu Y, Latha P, Munaswamy V, Reddy KR, Sreeprasad TSP, Sajanlal R, Pradeep T (2012) Effect of nanoscale zinc oxide particles on the germination, growth and yield of peanut. J Plant Nutr 35:905

Quaglia F, Barbato F, De Rosa G, Granata E, Miro A, La Rotonda MI (2001) Reduction of the environmental impact of pesticides: waxy microspheres encapsulating the insecticide carbaryl. J Agric Food Chem 49:4808–4812

Qureshi A, Kang WP, Davidson JL, Gurbuz Y (2009) Review on carbon-derived, solid-state, micro and nano sensors for electrochemical sensing applications. Diam Relat Mater 18:1401–1420

Ragaei M, Sabry A-KH (2014) Nanotechnology for insect pest control. Int J Sci Environ 2:528–545

Rai V, Acharya S, Dey N (2012) Implication of nanobiosensors in agriculture. J Biomate Nanobiotechnol 3:315–324

Rajakumar G, Abdul Rahuman A, Priyamvada B, Gopiesh Khanna V, Kishore Kumar D, Sujin PJ (2012) *Eclipta prostrata* leaf aqueous extract mediated synthesis of titanium dioxide nanoparticles. Mater Lett 68:115–117

Raliya R, Tarafdar JC (2013) ZnO nanoparticle biosynthesis and its effect on phosphorous-mobilizing enzyme secretion and gum contents in clusterbean (*Cyamopsis tetragonoloba* L.). Agric Res 2:48

Ramesh M, Palanisamy K, Babu K, Sharma NK (2014) Effects of bulk & nano-titanium dioxide and zinc oxide on physio-morphological changes in *Triticum aestivum* Linn. J Glob Biosci 3:415

Raskar SV and Laware SL (2014) Effect of zinc oxide nanoparticles on cytology and seed germination in onion. Int J Curr Microbiol Appl Sci 3:467

Rico CM, Majumdar S, Duarte-Gardea M, Peralta-Videa JR, Gardea-Torresdey JL (2011) Interaction of nanoparticles with edible plants and their possible implications in the food chain. J Agric Food Chem 59:3485–3498

Santhoshkumar T, Rahuman AA, Jayaseelan C, Rajakumar G, Marimuthu S, Kirthi AV, Velayutham K, Thomas J, Venkatesan J, Kim SK (2014) Green synthesis of titanium dioxide nanoparticles using Psidium guajava extract and its antibacterial and antioxidant properties. Asian Pac J Trop Med 7:968–976

Scott NR, Chen H (2003) Nanoscale science and engineering or agriculture and food systems. Roadmap report of national planning workshop 2002, 18–19 November, Washington DC

Sedghi M, Hadi M, Toluie SG (2013) Effect of nano zinc oxide on the germination of soybean seeds under drought stress. Ann West Uni Timisoara Ser Biol XVI:73

Sekhon BS (2014) Nanobiotechnology in agri-food production: an overview. Nanotechnol Sci Appl 7:31–83

Sharon M, Choudhary A, Kumar R (2010) Nanotechnology in agricultural diseases and food safety. J Phytology 2(4):83–92

Siddiqui MH, Al-Whaibi MH (2014) Role of nano-SiO_2 in germination of tomato (*Lycopersicum esculentum* seeds mill.). Saudi J Biol Sci 21(1):13–17

Silva AT, Nguyen A, Ye C, Verchot J, Moon JH (2010) Conjugated polymers nanoparticles for effective SiRNA delivery to tobacco BY-2 protoplast. BMC Plant Biol 10:291. 2229

Singh (2012): https://pdfs.semanticscholar.org/56d6/e6cf75867ad3b9a4fa1f38bfc46400ed1366.pdf

Singh S, Singh M, Agrawal VV, Kumar A (2010) An attempt to develop surface plasmon resonance based immunosensor for Karnal bunt (*Tilletia indica*) diagnosis based on the experience of nano-gold based lateral flow immune dipstick test. Thin Solid Films 519:1156–1159

Stampoulis D, Sinha SK, White JC (2009) Assay-dependent phytotoxicity of nanoparticles to plants. Environ Sci Technol 43(24):9473–9479

Sun G, Wheatley WB, Worley SD (1994) A new cyclic N-Halamine. Biocidal polymer. Indian Eng Chem Res 33:68–170

Suppan (2013): https://www.iatp.org/documents/nanomaterials-in-soil-our-future-food-chain

Suriyaprabha R, Karunakaran G, Yuvakkumar R, Rajendran V, Kannan N (2012) Silica nanoparticles for increased silica availability in maize (*Zea mays* L) seeds under hydroponic conditions. Curr Nanosci 8:902

Taylor NJ, Fauquet CM (2002) Microparticle bombardment as a tool in plant science and agricultural biotechnology. DNA Cell Biol 21(12):963–977

Torney F, Trewyn BG, Lin VS-Y, Wang K (2007) Mesoporous silica nanoparticles deliver DNA and chemicals into plants. Nat Nanotechnol 2:295

Tripathi et al (2018): https://www.ijcmas.com/special/7/Manikant%20Tripathi,%20et%20al.pdf

Ulrichs C, Mewis I, Goswami A (2005) Crop diversification aiming nutritional security in West Bengal: biotechnology of stinging capsules in nature's water bloom. Ann Tech Issue State Agri Technol Serv Assoc, pp 1–18

Upadhyaya H, Shome S, Tewari S, Bhattacharya MK, Panda SK (2015) Nanotechnology: Noval perspectives and prospects. McGraw Hill education India Pvt. Ltd, New Delhi, pp 508–512

Wang X, Han H, Liu X, Gu X, Chen K, Lu D (2012) Multi-walled carbon nanotubes can enhance root elongation of wheat (*Triticum aestivum*) plants. J Nanopart Res 14:1

Wright JE (1997) Formulation for insect sex pheromone dispersion. Patent number US 5670145 A 19970923

Wu L, Liu M, Liang R (2008) Preparation and properties of a double-coated slow-release NPK compound with superabsorbent and water retention. Bioresour Technol 99:547–554

Wu SG, Huang L, Head J, Chen DR, Kong IC, Tang YJ (2012) Phytotoxicity of metal oxide nanoparticles is related to both dissolved metals ions and adsorption of particles on seed surfaces. J Pet Environ Biotechnol 3:126

Yang L, Watts DJ (2005) Particle surface characteristics may play an important role in phytotoxicity of alumina nano particles. Toxicol Lett 158:122–132

Yan H, Mochizuki Y, Jo T, Okuzaki H (2011) Single-walled-carbon-nanotube based field effect transistors with biosensing functions for prostate-specific-antigen. J Bioequiv Avail 3:69–71

Yang F, Hong F, You W, Liu C, Gao F, Wu C, Yang P (2006) Influence of nano-anatase TiO2 on the nitrogen metabolism of growing spinach. Biol Trace Elem Res 110:179

Yang FL, Li XG, Zhu F, Lei CL (2009) Structural characterization of nanoparticles loaded with garlic essential oil and their insecticidal activity against *Tribolium castaneum* (Herbst) (Coleoptera: *Tenebrionidae*). J Agric Food Chem 57(21):10156–10162

Yao KS, Li SJ, Tzeng KC, Cheng TC, Chang CY, Chiu CY, Liao CY, Hsu JJ, Lin ZP (2009) Fluorescence silica nanoprobe as a biomarker for rapid detection of plant pathogens. Adv Mater Res 79-82:513–516

Yazdani F, Allahdadi I, AbasAkbari G (2007) Impact of superabsorbent polymer on yield and growth analysis of soybean (*Glycine max* L.) under drought stress condition. Pakistan J Biol Sci 10(23):4190–4196

Zambrano-Zaragoza ML, Mercado-Silva E, Gutiérrez-Cortez E, Castaño-Tostado E, Quintanar-Guerrero D (2011) Optimization of nanocapsules preparation by the emulsion diffusion method for food applications. LWT-Food Sci Technol 44:1362–1368

Zheng L, Hong F, Lu S, Liu C (2005) Effect of nano-TiO_2 on strength of naturally aged seeds and growth of spinach. Biol Trace Elem Res 104:83–91

Chapter 9
Understanding the Effect of the Interaction of Nanoparticles with Roots on the Uptake in Plants

Divya Singh and Arun Kumar

Contents

9.1 Introduction 278
9.2 Methodology 281
9.3 Effect of Soil Properties on Nanoparticle Characteristics 282
  9.3.1 Size of Pore Water/Soil 283
  9.3.2 Mobility of NPs in the Soil Column 284
  9.3.3 Feasibility of Aggregation in Pore Water/Soil 284
  9.3.4 Change in Surface Charge of Nanoparticle 285
  9.3.5 Dissolution of Nanoparticles in Pore Water/Soil 285
9.4 Nanoparticle Characteristics and Uptake in Edible Plants 286
  9.4.1 Effect of Nanoparticle Type on the Uptake in Edible Plants 287
  9.4.2 Effect of a Mixture of Nanoparticles on the Uptake in Edible Plants 288
9.5 Effect of Root Type on the Uptake 289
  9.5.1 Effect of the Role of Root Exudates on the Uptake of NPs in Roots 290
9.6 Nanoparticle Transport in Plants: Possible Routes 291
  9.6.1 Studies on the Effect of NPs on Multiple Generations of Plants 294
9.7 Summary and Conclusions 294
References 299

Abstract The wide expansion of nanotechnology in consumers, industrial, medical, and food products has raised a concern over the scientific community regarding their potential risk to human and the environment. Plant root is exposed to these nanoparticles (NPs) through sludge application and wastewater irrigation processes. The behavior and interaction of NPs in the soil, pore water, and rhizosphere play an important and central role in governing uptake. To this end, the current work critically reviewed the behavior of NPs in soil and root environment and tried to understand the effect of interaction on uptake and the possible pathways for NP uptake in edible plants. In addition, the current knowledge gaps in the current perspective on NP and soil interaction, NP-root interaction, etc. had been compiled after conducting the literature survey. The review of literature indicated that

---

D. Singh · A. Kumar (✉)
Department of Civil Engineering, Indian Institute of Technology, New Delhi, India
e-mail: arunku@civil.iitd.ac.in

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_9

knowledge gaps exist for the following components: (1) size of nanoparticles in soil, (2) mobility of NPs in soil, (3) aggregation in pore water and root, (4) change in surface charge in pore water and root environment, (5) effect of type of nanoparticle on uptake in edible plants, (6) type of plant on NP uptake, (7) mechanism of NP uptake in plants, and (8) multiple generational effects on NPs in plants. Based on the available literature, more studies on exposure of NPs to edible plants in environmentally relevant conditions are recommended. In addition, a multidisciplinary integrated approach to understand soil-nanoparticle-plant nexus is needed. The uptake of NPs in edible plants is directly dependent on its interaction with soil and root zone of plants. Therefore, this review highlighted on the status of knowledge, identified important data gaps, and suggested future research directions.

Keywords Nanoparticles · Plants · Uptake · Accumulation · Soil · Root · Food · Factors · Interaction · Environment

9.1 Introduction

Nanotechnology is a promising field of interdisciplinary research. Due to its unique properties, nanotechnology gives a wide array of opportunities in fields like medical, electronics, and agriculture (Rai and Ingle 2012). Among various applications in the agriculture sector, insect pest management through the formulations of nanomaterial-based pesticides and insecticides has enhanced agricultural productivity to a significant level (Ram et al. 2014). The application of nanotechnology to food industries due to promising potential benefits has improved food quality and food safety (Ram et al. 2014). Nanodevices are smart delivery systems that target specific sites and act as nanocarriers for the controlled release of chemicals. Nanodevices are manufactured as a device having dimensions on the scale of 1–100 nm (Monreal et al. 2016). These nanodevices have potential applications in the field of plant biotechnology and agriculture (Nair et al. 2010). Some nanotechnologies like nanoencapsulation can improve the existing crop management techniques and can significantly reduce the ill effects of herbicides and insecticides. In addition, nanocapsules can also improve the efficiency of herbicide by allowing the slow and constant release of the active substances (Ram et al. 2014). The nanoparticles (NPs) can also be loaded with herbicides and other chemicals to act as “magic bullets” and can target specific plant sites (Pérez-de-Luque and Rubiales 2009). Nanosensors are another gift from nanotechnology, which can detect microbes, humidity, and toxic pollutants at very-very minute levels. In addition, these nanosensors can sense and degrade pollutants and improve agricultural output with sustainable environmental protection (Baruah and Dutta 2009). In summary, nanotechnology has promising effects in the field of agriculture and has a promising potential to cope up with global challenges, like food safety and food security.

However, despite the potential benefits of nanotechnology in agriculture systems, there are various challenges which have to be taken care of (Mishra et al. 2017). The public concerns about the long-term effect, possible fate and transport, bioaccumulation, the effect on human life, and lack of regulatory framework challenge our complete acceptance of nanotechnologies in the agricultural sector.

As per PEN (Project on Emerging Nanotechnologies), the number of commercial products containing one or more than one NPs is growing day by day. Among a wide variety of NPs used, some of these NPs are used in a larger range of products and in higher volume. The manufactured NPs have distinctive surface properties, a large area-to-volume ratio, and size-dependent properties (Tourinho et al. 2012). These include silver NPs, titanium dioxide NPs, zinc oxide NPs, silica NPs, and carbon-based nanomaterials (Maurer-Jones et al. 2013). Another study revealed that the concentration of some of the NPs, such as titanium dioxide, fullerenes, silver NPs, zinc oxide NPs, and carbon-based nanotubes, are significantly higher in the environment (Hegde et al. 2016). In addition, enough evidence on the potential toxicity of these NPs on the environment is available in the literature (Dinesh et al. 2012) where exposure of the NPs can impact the function of soil, sediments, and microbial communities (Dinesh et al. 2012). The growing use of NPs in various products raises the demands for understanding on the uptake of NPs in edible plants.

Various uptake and toxicity studies during seed germination and full-scale growth of plants had been conducted. Table 9.1 summarizes the major areas in which review papers had been published on the nanoparticle- and plant-related studies. Previous studies have shown that environmental conditions, NP characteristics, and the variety of plants may influence NPs' interaction with plants. Physiochemical properties of NPs have an influence on their environmental uptake and toxicity. Characteristics of NPs, such as size, surface area, and morphology, may significantly affect physiological interactions between NPs and plants (Shin et al. 2015). It is well established that plant species and size, chemical composition and surface properties, and soil properties greatly influence toxicity, uptake, and transport of NPs in plant system (Garner and Keller 2014; Cornelis et al. 2014). The table clearly shows that no review had been performed on the effect of different factors on the uptake of NPs in edible plants. This is important information to know as it tells about the status of work done on factors affecting NP uptake in edible plants.

The objective of this review work was to understand the effect of the interaction of nanoparticles with roots on the uptake in plants. In this review, we have considered exposure of NPs containing water to edible plants and tried to understand various factors governing uptake of NPs in plants. Figure 9.1 shows the outline of this review work and highlights major factors governing NP uptake in edible plants. Edible plants can be exposed to NPs through various routes. Since it is virtually impossible to cover all the possible routes, we have selected the most probable route through which NPs can enter the food chain.

Table 9.1 Summary of review papers in the past decade

Title	Focus	Identified research gap/research needs
Nanoparticles: Their potential toxicity, waste, and environmental management (Bystrzejewska-Piotrowska et al. 2009)	(1) To highlight problems related to the uncontrolled release of NPs to the environment through waste disposal and (2) to introduce the topics of nanowaste and nanotoxicology to the waste management community	New methods for nanotoxicology and nanobiomonitoring
Interactions between engineered nanoparticles and plants: Phytotoxicity, uptake, and accumulation (Ma et al. 2010a)	Current knowledge on phytotoxicity/interactions of NPs with plants (at seedling and cellular levels) and compilation of data gap and research needs	(1) Effect of composition, particle size, and aggregation state affect the uptake kinetics, fate, and transport of NPs in plant, (2) effect of plant species and environmental factors on the uptake of NPs by plants
Interaction of Nanoparticles with Edible Plants and Their Possible Implications in the Food Chain (Rico et al. 2011)	NP studies on edible plants	Nanoecotoxicology and effects of NPs on the living components of ecosystems
Applications and implications of manufactured nanoparticles in soils: a review (Pan and Xing 2012)	The progress of research on manufactured nanoparticles and their implications for soils	Model-based on current production of NPs
Toxicity, Uptake, and Translocation of Engineered Nanomaterials in Vascular Plants (Miralles et al. 2012)	Evidence on the phytotoxicity of engineered nanomaterials	The mechanisms of penetration and interaction of NP plants
Toxicity of Engineered Nanoparticles in the Environment (Maurer-Jones et al. 2013)	Current understanding of NP phytotoxicity, both in vitro and in vivo, and possible mechanisms for bioaccumulation	(i) Toxicity assessment in complex ecosystems, (ii) detecting NPs that are similar in chemical composition to natural particulate matter, (iii) characterizing the NPs in a complex, natural environment
Emerging patterns for engineered nanomaterials in the environment: A review of fate and toxicity studies (Garner and Keller 2014)	Identification of the emerging trends in fate and toxicity of engineered nanomaterials under various environmental conditions	Not identified
Barriers, pathways, and processes for uptake, translocation, and accumulation of nanomaterials in plants – Critical review (Schwab et al. 2015)	Information on the currently known engineered nanomaterial uptake, translocation, and accumulation processes in plants	Estimation of uptake rates, the size exclusion limit of the apoplast, effect of plant physiological features on the uptake

(continued)

Table 9.1 (continued)

Title	Focus	Identified research gap/research needs
Environmentally relevant approaches to assess nanoparticles ecotoxicity: A review (Bour et al. 2015)	Studies on engineered NPs using environmentally relevant exposure methods	Development of methods for detection and quantification of NPs in natural environments and assessment of the fates and effects of NPs
Environmentally relevant approaches to assess nanoparticles ecotoxicity: A review (Bour et al. 2015)	Review on NPs using environmentally relevant exposure methods	Lack of NP fate and effects in environmental conditions and additional studies of consumer products containing NPs
Impact of nanoparticles on human and environment: A review of toxicity factors, exposures, control strategies, and future prospects (Sajid et al. 2015)	Characteristics of NPs, which form the basis of their toxicity and possible routes of exposure of NPs to the human body	Development of research methods to explore toxicity of all kind of NPs
Silver and titanium dioxide nanoparticle toxicity in plants: A review of current research (Cox et al. 2016)	Understanding the effect of silver and titanium dioxide NPs on plant species	Understand the interaction between NPs and root hair cells
Effect of metal and metal oxide nanoparticles on growth and physiology of globally important food crops: A critical review (Rizwan et al. 2017)	Effects of NPs on agricultural crops at biochemical, physiological, and molecular levels	NP mechanisms in plants and soil
Uptake and Toxicity of Nanomaterials in Plants (Dev et al. 2017)	Mechanisms of interaction of NPs with plants (focus: uptake, translocation, and toxicity behavior at physiological, proteomic, transcriptomic, and metabolomic level)	Not identified

Keywords: Nanoparticles, Toxicity, Plants, Duration 2007–2017) (NP, nanoparticles
NP nanoparticles

9.2 Methodology

This review work summarizes and evaluates the present knowledge on the factors affecting NP toxicity and uptake in edible plants with considerations on the NPs having highest chances of presence in the environment. The review of the literature was carried using studies published in the past decade (2007–2017), and findings were presented in three major sections, i.e., the fate of NPs in suspension, the fate of NPs in soil, and the fate of NPs in plant root environment. This review work identified data gaps and proposed research directions to have a better understanding of NP uptake in edible plants. Keywords like “nanoparticle,” “plants,” “size, surface

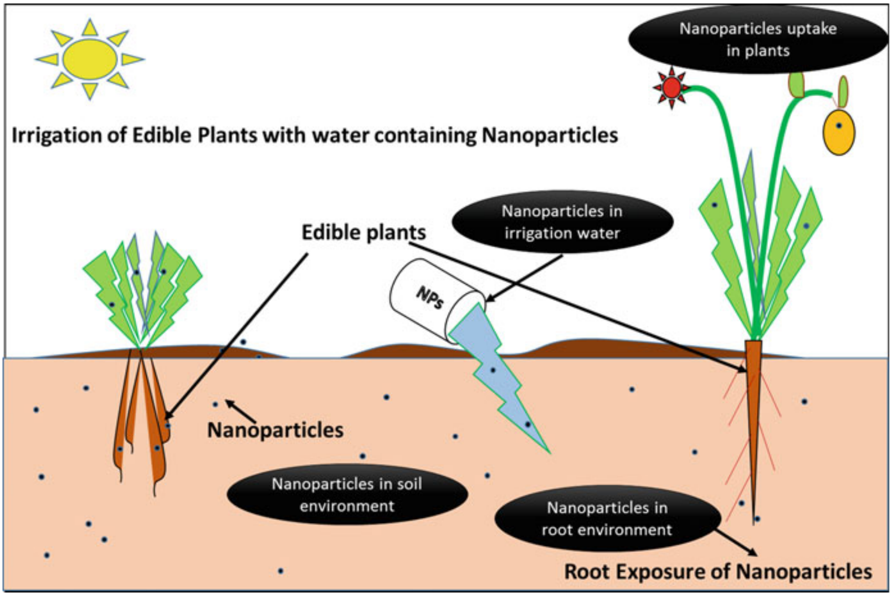


Fig. 9.1 Outline of the review conducted (NP, nanoparticles). It indicates that nanoparticles present in water interact with soil and are taken up by plant roots. NP uptake by plants and effect of NPs on plants depend on its interaction with soil and root structure

charge, dissolution, aggregation," and "uptake" were searched in databases, such as Science Direct and Google Scholar, to obtain relevant papers. The findings of the review are summarized below.

9.3 Effect of Soil Properties on Nanoparticle Characteristics

Physicochemical properties of NPs, like size and shape, solubility, and surface charge, determine the possible behavior of NPs in the soil environment. These properties of NPs will, in turn, govern aggregation/agglomeration, sorption to soil surfaces, and dissolution to the ions (Tourinho et al. 2012). The following sections present the compilation of the factors affecting NP properties (size, mobility, aggregation, surface charge) in soil media. Figure 9.2 summarizes the factors affecting NP size, mobility, aggregation, and dissolution in aqueous and soil media.

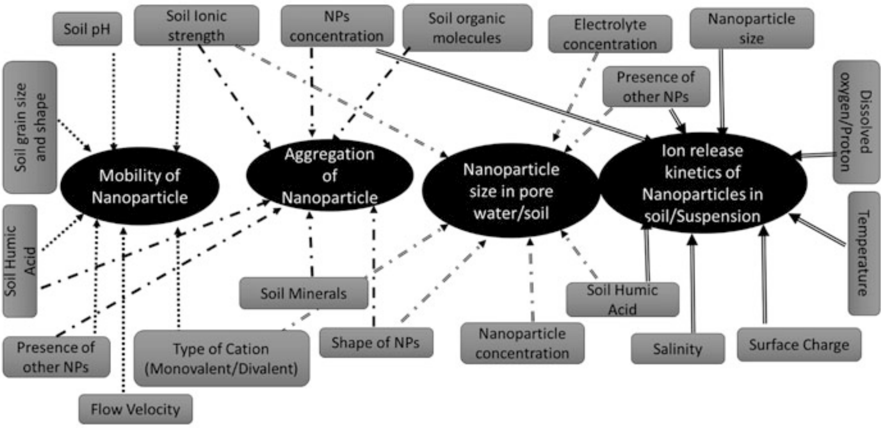


Fig. 9.2 A schematic showing interconnection between the factors affecting the fate of NPs in soil (NPs, nanoparticles). Different soil-related parameters, water-related parameters, and NP characteristics affect the fate of NPs in soil and its chance of uptake by plants

9.3.1 *Size of Pore Water/Soil*

Once released into the environment, NPs move in different media like water, soil, and sludge. Studies on NPs and plants have shown that the size of NPs plays an important role in determining uptake. Most NPs have a tendency to get aggregated, and this plays a major role on their sedimentation rates (Keller et al. 2010). The distribution of NPs in different plant tissues has been shown to be dependent on size (Reidy et al. 2013). Size of NPs is affected by water and soil chemistry. In addition, the aggregate size is influenced by ionic strength (IS) and pH (Conway et al. 2015). One study on the uptake of CeO_2 NPs by wheat, pumpkin, and sunflower plants is grown in hydroponic media revealed that the contribution of dissolved Ce uptake was more for NP size smaller than 10 nm due to their higher dissolution rate. One more interesting finding was that no translocation of Ce from roots into shoots was found for a size lower than 20 nm (Schwabe et al. 2015). In summary, size has a strong influence on internal uptake of NPs in edible plants. Size also governs the potential of NP movement from root to shoot portions of the plants. In spite of size being an important factor for understanding uptake in plants, there is still a paucity of data on edible plants. In addition to this, change in size due to different soil-dependent factors (like pH, organic matter content) needs further detailed investigations, so that uptake of NPs by roots and its translocation can be predicted.

9.3.2 Mobility of NPs in the Soil Column

The mobility of NPs in soil is an important factor which determines its bioavailability to the plants. It is found that the plant more readily takes up NPs with higher mobility. Despite the fact that soil is known to be exposed to various natural and manufactured NPs, there is still limited information available on the potential mobility of NPs in soil under environmental conditions. Previous studies have shown that the ionic strength and type of cation present in the soil/sand have a significant effect on the mobility of NPs (Saleh et al. 2008). Higher ionic strength limits the mobility of NPs in the soil column. In another study on the transport of cerium oxide NPs in silica, the concentration of divalent cations, electrolyte concentration, pH, and concentration of NP in media also influence the mobility of NPs. Ionic strength was found to play a major role in mobility of NPs in soil media. An increase in attachment efficiency and particle size was found at lower ionic strengths (1–10 mM KCl). An increase in attachment efficiency with increasing particle size was observed (Pelley and Tufenkji 2008). Apart from ionic strength, the presence of natural soil organic matter also plays a crucial role in governing NP mobility in aqueous media (Keller et al. 2010). In case of TiO_2 NPs, humic acid content and pH of soil were reported to play important roles in affecting NP mobility in the soil column. The pH of soil was found to determine the interaction of NPs with the soil/sand surface (Chen et al. 2012). Graphene oxide NP mobility in sandy soil was found to be dependent on soil texture, flow velocity, ionic strength, and humic acid content. This study also mentioned that humic acid enhances the mobility, while higher ionic strength limited the mobility of NPs in soil (Qi et al. 2014). The translocation of NPs in the living systems can be decreased by increasing the thickness of the biological barrier and decreasing the mobility (Birbaum et al. 2010). The analysis of findings of literature indicates that NPs are quite mobile in the soil, and their movements in soil column under given environmental conditions need to be understood properly to determine their potential environmental risks. Mobility seems an important factor when assessing bioavailability to plants, but most of the studies had been found in soil column under laboratory conditions. In addition to this, the effect of environmental factors, mainly soil properties, on mobility under given environmental conditions is missing from the literature and, thus, need to be studied.

9.3.3 Feasibility of Aggregation in Pore Water/Soil

Aggregation means a cluster of NPs of any form. The NPs can be aggregated with soil, bacteria, and among themselves. Aggregation of NPs depends on different NP-related characteristics, such as surface charge, size, concentration, and shape. Aggregation of NPs was reported to be higher at high NP concentration due to the higher chances of collisions between particles. On the contrary, the presence of organic molecules is a barrier to the aggregation process of NPs (Keller et al. 2010).

Due to gravity, heavier aggregates have a tendency to settle rapidly. Another study mentioned that aggregation kinetics is controlled by ionic strength and total organic content of soil as well (Conway et al. 2015). Another study mentioned that anionic charges on humic substances play a major role in the aggregation and disaggregation of ZnO NPs (Mohd Omar et al. 2014). The aggregation property of NPs determines their fate and uptake in the environment. For TiO_2 NPs, a combination of salt concentration and ionic strength influences aggregation formation in the media (Shih et al. 2012). Further, another study reported that the particle diameter and salt concentration governed aggregation of the nC60 particle as well. Reports say that the nC60 particle diameter was observed to be minimal in the presence of NaCl but increased by more than sevenfold in the presence of $CaCl_2$ (Wang et al. 2008). Apart from the abovementioned factors, aggregation properties were also found to be independent of pH (Keller et al. 2010). Presence of other metals in soil as soil minerals can also promote NP aggregation (Cornelis et al. 2014). The soil components, such as bulk soil, root zone, and pore water, also affect aggregation. For example, another study found that soil pore water consisting of electrolytes affects aggregation of NPs in soil media and helps in reducing the internal uptake of NPs in plants as micron-size aggregated NPs cannot pass through the plant cell (Lee et al. 2008). The interaction of aggregated NPs with the plant root surface is different from non-aggregated NPs. Still, limited literature is available on the interaction of aggregated NPs with plant root surface. As soil is a heterogeneous mixture of various components, the influence of all the factors of aggregation properties of NPs needs detailed understanding.

9.3.4 Change in Surface Charge of Nanoparticle

The surface charge of NPs is an important characteristic which along with factors, like pH, ionic strength, organic content, etc., affects the stability of NPs in soil media (Tourinho et al. 2012). It is said that toxicity of NPs is dependent on many factors, like size, shape, etc., but the surface charge is considered as one of the most important factors (Dinesh et al. 2012). Therefore, the surface charge is the key to controlling NP behavior in soil media and subsequently their transport and uptake in living organisms. Among all NP-related parameters, the factors affecting the surface charge of NPs in soil media are poorly understood, and thus, it requires an immediate attention.

9.3.5 Dissolution of Nanoparticles in Pore Water/Soil

Once released into the environment, the NPs can remain as NPs or may release ions in their environment. Dissolution is an important process, which controls the behavior of NPs in suspension. Dissolution of NPs into ions can be governed by the size of the NP. Some of the parameters, like the ionic strength of media, NP size, shape and surface charge, pH of media, the concentration of dissolved oxygen, temperature, and complexing agents like organic matter, either enhance or suppress NP dissolution in the media. Among all, NP size is one of the most important parameters that control dissolution (Elzey and Grassian 2010; Conway et al. 2015). Some studies also say that the pH of the solution and surface charge are among the two important factors governing stability of NPs in aqueous solution (Fang et al. 2009). Some other studies identified the remarkable effect of surface coating on NP dissolution in ions. This study also highlighted the effect of ionic strength on dissolution (Li and Lenhart 2012). Bare NPs were found to be non-stable and have higher tendency to give ions as compared to coated NPs in soil media (Hedberg et al. 2015). In addition to these NP-related parameters, other soil properties, such as soil organic matter, clay content, and soil moisture and root exudates, affect NP dissolution in the soil. Among all, soil pH appears to be one of the key factors affecting the behavior of metal NPs in soil (Read et al. 2016). Temperature also plays a major role in determining the degree and rate of NP dissolution (Kittler et al. 2010). The surface area of NPs was also found to play a major role in determining the degree of dissolution of NPs with higher dissolution rate for smaller particles (Waalewijn-Kool et al. 2013).

9.4 Nanoparticle Characteristics and Uptake in Edible Plants

The NPs of different sizes display different behaviors toward the plants. For example, a study on tobacco plant reported internal uptake of gold NPs in the plant was found to be size-dependent. The smaller-size gold NPs (3.5 nm) were taken up internally, while 18 nm size NPs remained agglomerated on root surfaces. Gold NPs (3.5 nm) also resulted in leaf necrosis (Sabo-Attwood et al. 2012). In another study, the effect of two different sizes of CeO_2 NPs was also studied on cucumber plants where the higher content of Ce was noticed for 7 nm CeO_2 in root and shoot portions than 25 nm CeO_2 NPs for exposure concentrations of 2, 20, and 200 mg/L (Zhang et al. 2011). In some cases of seed germination studies, size has not shown any clear inhibition. For example, exposure of AgNPs (concentration 0–100 mg/L and size 1–20 nm) to barley and flax seeds has not shown any clear effect on germination of seeds (El-Temsah and Joner 2012). In addition, there is evidence that the smallest-size TiO_2 NPs were observed to be accumulated in roots and distributed in wheat plants; however, it did not affect germination of wheat seeds (Larue et al. 2012).

The NPs have a tendency to aggregate on soil surface due to some physical forces or strong bond and hence are available for uptake in plants. One study states that soil colloids can act as a carrier of strongly adsorbed NPs onto the soil surface (e.g., soil clay material). For example, in ZnO NP-treated corn plants grown in soil media, aggregated ZnO NPs was observed to be present on the epidermis of the root and then later move to the endodermis through the symplastic pathway (Zhao et al. 2012a). Another study found that electrolyte present in soil pore water affects aggregation of NPs in soil media (Lee et al. 2008) and thus reduces their internal uptake by plants. It further helps in reducing phytotoxicity of NPs to plants in soil media (Lee et al. 2012). A comparison of fate and toxic effect of NPs and bulk is also an interesting dimension to study as bulk materials show higher uptake than their NP counterparts (Dimkpa et al. 2012).The NPs and ions display a different level of uptake in plants (Lin and Xing 2008). Various environmental factors govern NP-ion exchange. Exposure of sweet potato to ZnO, CuO, and CeO_2 NPs and their ion counterparts (equivalent amounts) (Zn^{+2}, Cu^{+2} and Ce^{+4}, and metals) was observed to be accumulated in both the peel and flesh of the sweet potato tubers with the highest concentration of Zn followed by Cu. This study also stated that added NPs underwent dissolution in soil media to release their ions before accumulation (Ebbs et al. 2016b). Carrot (*Daucus carota*) grown with ZnO, CuO, or CeO_2 NPs and Zn^{2+}, Cu^{2+}, or Ce^{4+} in sand media resulted in higher metal content for the ionic treatments than for the NPs in root portion (Ebbs et al. 2016a). In addition, NPs showed reduced accumulation than the ionic treatments in the edible tissues of carrot (Ebbs et al. 2016a).

The internalization and transport of NPs in plants can be understood based on the physicochemical characteristics of NPs near the plant roots. The abovementioned studies demonstrated that NP characteristics, like size, surface charge, mobility, and dissolution, play an important role in internal uptake within edible plants. In spite of the proven fact, studies on the effect of NP properties on uptake are limited. The behavior of NPs in the presence of other NPs remained unexplored. The NPs had been found to interact with other NPs in an antagonistic and synergistic manner (Singh and Kumar 2016), but still more studies in realistic environmental conditions are needed.

9.4.1 Effect of Nanoparticle Type on the Uptake in Edible Plants

Different manufactured NPs have different properties that influence their uptakes in plants. Several studies have exposed edible plants with different NPs at the same concentration level and observed different levels of internal uptakes of different types of NPs exposed. For example, when cucumber was grown in soil media in the presence of CeO_2 and ZnO NPs (400 and 800 mg/kg loadings, respectively), higher bioaccumulation was observed for Zn (110 mg/kg dry weight) than Ce (1.27 mg/kg dry weight) in the fruit portion of the plant (Zhao et al. 2013). Another study (Song et al. 2013) compared uptakes of TiO_2 NPs and Ag NPs in tomato plants and observed that at the highest exposure concentration of 5000 mg/kg soil, the Ti and Ag metal contents were found to be 163 and 653 mg/kg seed weight, respectively. This study also reported that Ag NPs were observed to be uptaken at a higher rate than TiO2 NPs. Another study on exposure of sweet potato (*Ipomoea batatas*) with

CuO, ZnO, and CeO_2 NPs (concentration range: 100, 500, or 1000 mg kg/dry weight) reported accumulations of 90 mg/kg Zn, 24 mg/kg Cu, and 5 mg/kg of Ce in unpeeled tumor of sweet potato (Ebbs et al. 2016b). Exposures of CuO and ZnO NPs to sand-grown wheat plants (concentration: 500 mg/kg sand) resulted in the accumulation of Cu (19 mg/kg) and Zn (88 mg/kg) in shoot portions of the plant (Dimkpa et al. 2012). Irrigation of tomato plant with metal oxides (CeO_2, Fe_3O_4, SnO_2, TiO_2) and metallic (Ag, Co, Ni) NPs resulted in metal accumulations (mainly for the case of metal oxide-based NPs) in the root portion of tomato and metal accumulations in both root and shoot portions (for the case of metal-based NPs) (Vittori Antisari et al. 2015). CuO and ZnO NPs were exposed to spinach plants in soil media, and higher uptake was observed for ZnO NPs at highest exposure concentration (Singh and Kumar 2016). Another study exposed TiO_2 NPs and multi-walled carbon nanotubes (MWCNTs) to red clover and wheat, grown in soil media in a pot, and reported limited mobility of TiO_2 and multi-walled carbon nanotube NPs in the soil. Ti uptake and multi-walled carbon nanotube uptake in plants were found to be independent of the exposure concentration (Serag et al. 2011). All the mentioned studies suggest that the NP uptake in plants is highly dependent on the type of NP exposed to the plants, and thus NP and plant interaction has to be understood for different combinations of plants and NPs.

9.4.2 Effect of a Mixture of Nanoparticles on the Uptake in Edible Plants

The effluent and biosolids from wastewater treatment plants contain a complex mixture of organic matter and inorganic salts (Ma et al. 2014). The NPs present in the soil might encounter other pollutants, including other NPs present in the vicinity. The NPs may interact among themselves based on their size, shape, chemical composition, solubility, surface area etc. The mixture of NPs may interact either in an additive or synergistic or antagonistic manner which, in turn, affects the internal uptake of NPs in edible plants (Jośko et al. 2017). A study focusing on the effect of a mixture of NPs on plant growth and their uptake in plants is important, as there is a chance of co-occurrence of more than one type of NPs in water, which may present a situation where plants are exposed to more than one type of NPs simultaneously. An increase in the widespread application and use of NPs will inevitably lead to the co-occurrence of different NPs in the environment (Yu et al. 2016). In general, the environment is generally exposed to complex mixtures of contaminants. However, most of the studies have mainly focused on understanding the effect of single contaminants on plants under laboratory conditions (Pavlaki et al. 2011). Therefore, studies focusing on understanding the effects of the mixture of NPs on plants rather than the effect of a single NP reflect ecosystem pollution more realistically. Very few studies on understanding the effect of a mixture of NPs on plants are present in literature. A study assessed the effect of mixtures of NPs, believed to be toxic (ZnO

NPs and CuO NPs) and nontoxic NPs (TiO_2 NPs, Cr_2O_3 NPs and Fe_2O_3 NPs), on four plant species, *Lepidium sativum*, *Linum usitatissimum*, *Cucumis sativus*, and *Triticum aestivum*, and observed that the mixtures of NPs were found to be significantly lesser toxic than individual NPs (Jośko et al. 2017). Another study on spinach, exposed to a single and binary mixture of CuO and ZnO NPs, suggested a significant reduction in uptake of NPs as compared to control spinach plants (Singh and Kumar 2016). Until date, most of the studies have been conducted with the combination of metal ions, salts, and NP-metals. However, the effect of a mixture of NP with NP/metal ions on the uptake in edible plants needs further research.

9.5 Effect of Root Type on the Uptake

The NP with a unique property of making stable colloidal suspensions in water has resulted in growing concern over possible accumulation in edible parts of plants and its subsequent effect in the food chain. All edible plants are categorized into monocot and dicot plants with the main difference in the positioning of xylem and phloem. Monocot roots have their vascular bundles arranged in the form of a ring. Dicot roots have their xylem present in the center of the root and phloem present outside the xylem. Manufactured NPs present in soil may accumulate at the external root surfaces of transpiring plants and are transported to other parts of the plant as well. As xylem structures determine the speed of water transport, different xylem structures have been observed to demonstrate different uptake kinetics of nanoparticle (Ma et al. 2010b). Another study mentioned that monocot roots have siderophores which result in binding/adsorption of metals (Jacob et al. 2013). In addition, a previous study mentioned that monocots exhibit a lesser tendency to uptake NPs due to their root structure.

Studies have also reported the effect of the presence of root exudates on metal uptake in plants. For example, a study found that dicot plant root has better ability to uptake metals from the soil than monocot plant root due to the differences in root exudates (Pappas et al. 2017). The possible reason behind the difference of behavior was attributed to the presence of organic acid in root exudates of dicot which might have resulted in lowering of pH in the vicinity of root and, thus, in solubilizing metals (Pappas et al. 2017). Another report on the toxicity of NPs on mung bean (dicot) and wheat (monocot) showed that bean was observed to be more sensitive to NP toxicity than wheat due to differences in their root anatomy. Mung bean has large primary root and several smaller lateral roots, while wheat is a monocot with numerous small roots without a primary root (Rico et al. 2011). Another study on wheat (monocot plant) mentioned that different plant species behave differently regarding accumulation and excretion of metals, which can also be found for the case of NPs as well (Cifuentes et al. 2010). Similarly, many different studies have reported differential uptakes of NPs in monocot and dicot plants (Jacob et al. 2013; Wang et al. 2017; Ruffini Castiglione et al. 2011; Ma and Quah 2016). Overall, analysis of these studies indicates that uptake of NPs in plants differs due to the difference in root characteristics, root morphology, and anatomy. These observations indicate that uptake of NPs in the plant might also depend on root type, and thus plants with different types of root might uptake NPs differently. The information that dicot plants are expected to uptake NPs more than monocot plants suggests that irrigation using NP-containing wastewater can be explored for dicot plants than monocots as this situation is expected to result in lesser uptake of NPs in plants and, thus, lesser toxicity to plants as well.

9.5.1 Effect of the Role of Root Exudates on the Uptake of NPs in Roots

The plant roots exudate a wide variety of organic compounds, such as sugar, organic acids, polysaccharide, and enzymes, and account for the largest source of soil carbon. These exudate compounds help plants and microorganisms in various ways. The root exudates function as plant defense system below the ground (Martinoia and Baetz 2014). It consists of a wide variety of chemical secretions from the root which regulate soil microbial communities in the vicinity of the plant. This further helps in the establishment of symbiosis which benefits plant growth (Winkel-Shirley et al. 2001). In addition to this, the exudates maintain and support a highly specific microbial community in the rhizosphere of a particular plant type (Badri and Vivanco 2009). The rhizosphere of the plant also houses a rich microbial community (more than 1000 bacteria/g soil) (Vacheron et al. 2013). The monocot and dicot plants have different characteristics of root exudates due to their different abilities of metal accumulation. The difference in the type and nature of root exudates also governs the uptake of ions and NPs in edible plants by facilitating aggregation and internal uptake (Schwab et al. 2015). Some studies have illustrated the role of root exudates in facilitating NPs' internal uptake in edible plants. A study on cucumber states that root hairs and root cells secrete polysaccharide-rich mucilage, which may contain negative charge. Some of the NPs are positively charged (at neutral pH) and thus can get attracted to the negatively charged root. The electrostatic attraction results in physical adsorption of NPs on the root surface. Another study on ceria NPs with cucumber plants states that the root exudates excreted organic acids and other reducing substances, which can play important roles in NP dissolution. The released ions are accumulated on the root surface and intercellular spaces and can get accumulated in shoot portions of the plants (Zhang et al. 2012). Quantum dots were also found to combine and react with plant root due to the presence of protein, amino acids, and sugars in root exudates (Al-Salim et al. 2011). The root exudates can modify the surface of the NPs in soil (Dimkpa et al. 2013). One more study confirms the role of root exudates in adsorption and dissolution of NPs, and their subsequent transfer to root and shoot portions of the plant is facilitated in the presence of hydrated polysaccharide secreted from the root (Ma et al. 2010c).

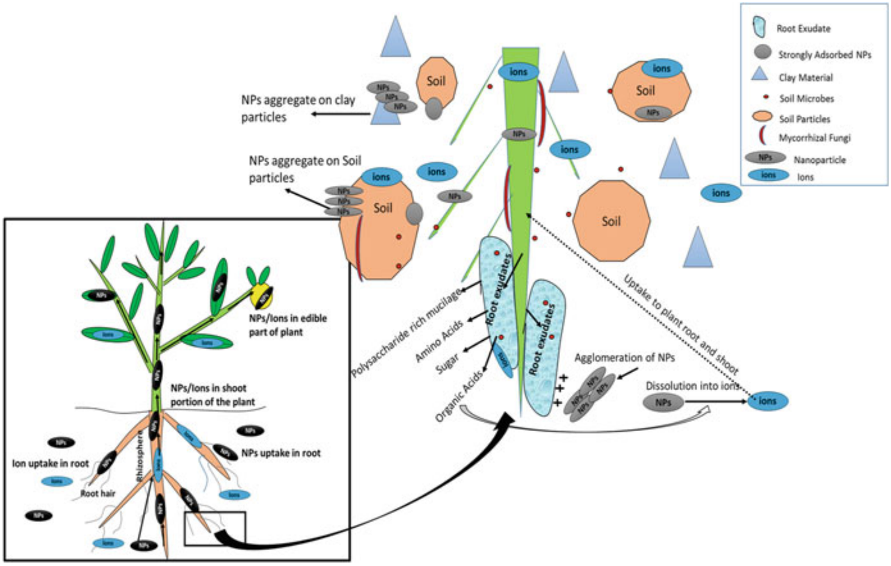


Fig. 9.3 A schematic showing possible interaction of NPs with rhizosphere of the plant. Root hairs are exposed to NPs, ion, and other soil-related constituents. NPs interact with each other and with soil and pore water constituents, which finally affect NP's fate in soil and NP's uptake by root hairs. The image in the inset shows a big-picture schematic of the interaction of NPs with root and its upward transport within roots and other parts of plants

Monocots and dicots have different morphology and anatomy of root and thus have a difference in the nature of root exudates. Roots have been shown to secrete different types of root exudates for obtaining metal nutrients from the soil (Judy et al. 2012). The monocot plant secretes siderophores from their roots as exudates and is able to maintain the negative charge in the rhizosphere at neutral pH and low ionic strength. This, in turn, helps in agglomeration of NPs in the presence of root exudate (Dimkpa et al. 2013). Therefore, it can be concluded that the differences in type and amount of root exudates among plant species might also affect uptake of NPs in plants, either by facilitating uptake in plants or by inducing NP aggregation (Judy et al. 2012). Figure 9.3 shows the possible interaction of NPs with rhizosphere of the plant in the presence of root exudates.

9.6 Nanoparticle Transport in Plants: Possible Routes

The uptake of nanoparticles in edible plants depends on many factors like plant species, the age of the plant, and nanoparticle properties (nature of nanoparticles, size, surface charge, etc.). The nanoparticles can get accumulated in the root, shoot leaves, and edible parts based on plant- and NP-based properties (Raliya et al. 2015). There is still a paucity of data on understanding nanoparticle uptake, translocation to

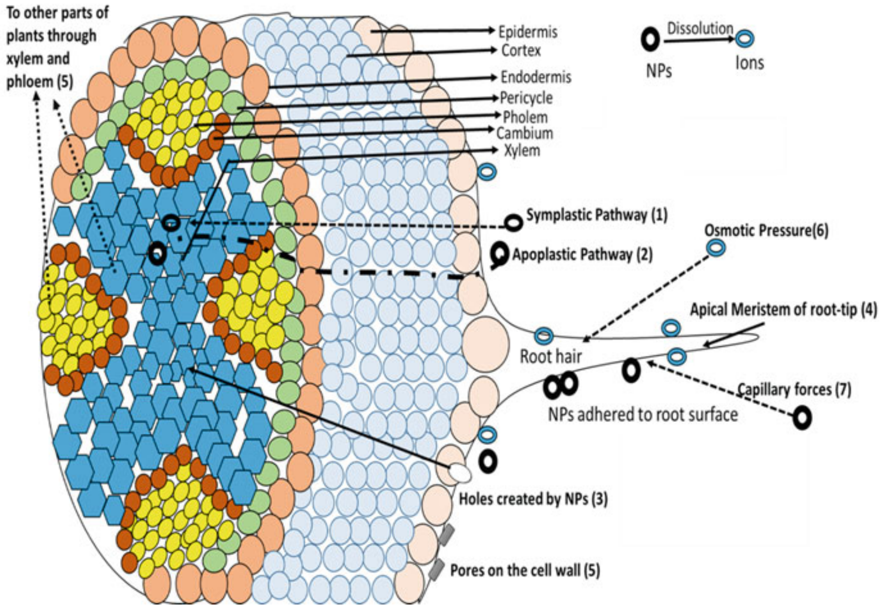


Fig. 9.4 A compilation of different literature-reported proposed mechanisms for nanoparticle (NP) internalization in plants through the root. Mechanisms are (1) symplastic pathway, (2) apoplastic pathway, (3) entry through holes created by nanoparticles, (4) apical meristem of root tip, (5) entry through pores on the cell wall, (6) entry to other parts of plants through xylem and phloem, (7) entry through interaction with capillary forces

edible parts, and biotransformation of nanoparticles in edible plants. Although our understanding of plant-nanoparticle interactions has advanced in the past decade, the mechanisms of nanoparticle transport from the root to shoot and portions of the plant's tissues are still lacking. Many theories had been proposed (described below), but still a clear understanding is missing.

Figure 9.4 shows the possible ways through which NPs can enter inside the plant through the root zone. The various pathways were denoted as 1, 2, 3, 4, 5, 6, and 7 in the figure. Plasmodesmata are the membranous structure, which connects plant cell through the cytoplasm. This controls the movement of different molecules from one cell to another, which is called as symplastic pathway (pathway #1).

Apoplastic pathway (pathway #2) includes the movement of molecules through the extracellular spaces outside the plasma membrane, cell wall, and intercellular spaces (Milewska-Hendel et al. 2017). The NPs can penetrate the cell wall and membrane of the root epidermis and can then enter the xylem portion of the plants. For example, Zhao et al. (2012a) studied the uptake of Zn and ZnO NPs in corn plants exposed in sandy-loam media and reported that the soil colloids acted as carriers of strongly adsorbed NPs, and soil clay minerals helped in the aggregation of Zn/ZnO NPs. These aggregated NPs penetrated the root epidermis and cortex (through the apoplastic pathway) and xylem (through the symplastic pathway)

(Zhao et al. 2012a). In another study, cerium oxide NPs were observed in plant tissues implying that NPs can move along with the water flow to other parts of the plant once it enters into the vascular bundle of the plant (Zhang et al. 2011). Another study says that CeO_2 NPs might have entered through the apoplastic pathway as aggregates were found in cell walls of the epidermis and cortex (as observed using a confocal microscope) and vascular bundles (as observed using a micro X-ray fluorescence) (Zhao et al. 2012b). In another study, the movement of gold NPs in barley was investigated by puncturing the root and directly applying the NPs in root cells. It indicated no translocation, suggesting no apoplastic and symplastic movements in barley plants (Milewska-Hendel et al. 2017). The plants follow different pathways for the uptake of NPs. The apoplastic pathway in maize was identified for movement of quantum dots (Hu 2010), and symplastic pathways were identified for wheat and maize (for silica NPs) (Sun et al. 2014). A combination of apoplastic and symplastic pathways was observed in rice during exposure to carbon NPs (Lee and Lu 2011). Plants, like barley, were not reported to uptake gold NPs regardless of their size and concentration (Milewska-Hendel et al. 2017).

NPs can increase the permeability of plant cells by creating “holes” on root cells (pathway #3). The NPs are also known for creating nanoscale holes on the membrane (15–49 nm in diameter) which facilitate NPs’ internal uptake in plants (Zhu et al. 2012). The smaller NPs have a capability to create new root pores due to their higher surface reactivity, resulting in high mineral and nutrient uptake (Raliya et al. 2015). Another study (Lin and Xing 2008) reported that ZnO NPs might have created holes (pathway #3), leading to increase in the permeability of plant cell walls and thus increase in entry and transport of NPs into the cell via plasmodesmata. The apical meristem (pathway #4) part of the plant has high porosity due to active cell division. In addition, this part also facilitates faster transport of NPs due to underdeveloped Casparian strip and easy diffusion to xylem vessels (Zhang et al. 2011). In addition to the abovementioned mechanisms, the NPs can be transferred to other parts through the vascular system (pathway #5). For example, Lin et al. (2009) observed that the C70 NPs can share the vascular system of the plants and are transported along with water and nutrients. Further, they also observed that C70 NPs were found to leak into nearby tissues after aggregation within the vascular system. The vascular system is responsible for the bio-distribution of NPs in plants. The soil-mediated NPs exposed are transported to the xylem in a unidirectional way (Raliya et al. 2015). Another study (Rico et al. 2011) mentioned that NPs undergo bio-transformation using humic acid and root exudates and are internally taken up by the root.

The pore in the cell wall of a living plant cell is also one of the important entry points for NPs (pathway #6). It is reported that the diameter of the pores can limit entry of NPs. The diameter of a typical pore in the cell wall of plant cells is 3.5–5 nm. The NPs having size less than 3.5–5 nm can easily get access to the plant system (Lin and Chen 2009). This provides a sieving property to the plant cells. If the size of NPs is larger than the pore of the root, NPs form an aggregate on the surface (Siddiqi and Husen 2017). Another study (Larue et al. 2012) observed that the TiO_2 NPs above a threshold diameter of 140 nm were not observed to be accumulated in wheat roots.

Further, this study also noted that TiO_2 NPs above 36 nm could not reach the stele and cannot be translocated to the shoot portion. Other factors like osmotic pressure (pathway #7) and capillary forces (7) can also play a major role in the upward movement of NPs in plants (Lin et al. 2009). It appeared that the movement of NPs inside the plant is specific to plant type and NP type exposed. As different plants have their specific root morphologies and anatomies, the cellular structure and cell wall pore size are different. The uptake properties of plants are highly variable, and literature does not show any explicit mechanism of translocation of NPs in plants. Very clearly, the interaction mechanism between plants and NPs is still not clear, and thus, this aspect deserves an in-depth investigation. There are various possible routes for the entry of NPs inside the plants, and various routes might be involved in NP transport simultaneously, which makes it difficult to understand as per the available knowledge. Thus, a detailed study for explicitly bringing out the effects of each pathway is required.

9.6.1 Studies on the Effect of NPs on Multiple Generations of Plants

Nanomaterials are present in a number of commercially available products, but there are uncertainties as to whether the unique properties that support their commercial usages may also pose potential health risks. The trans-generational effects in edible plants are necessary for understanding the genetic effects of NPs and subsequent effect on progenies. Information is missing concerning the influence of nanomaterials on the overall reproductive outcome and trans-generational effects in animals and plants (Poma et al. 2014). Although no study had been found focusing on multiple generation effects of NPs on edible plants, Table 9.2 compiles the available literature on multiple generation effects of NPs in edible plants.

The multigenerational and long-term exposure to NPs altered the plant physiological and biochemical responses in subsequent generations of plants. The studies on the effect on multiple generations of the plants due to NP exposure are still lacking in the literature. Effect of a mixture of NPs on multiple generations of plants is another important aspect with limited knowledge. The potential impacts of these processes on both food safety and the environment are important subjects to understand.

9.7 Summary and Conclusions

The edible plants can be exposed to NPs through sludge application and wastewater irrigation. The uptake of NPs in edible plants is governed by many factors. Some factors are NP-based (size, shape, charge, the rate of dissolution into ions,

Table 9.2 Compilation of findings of studies on trans-generational effect of nanoparticles (NPs)

Focus/reference	Plant/nanoparticles/ concentration/factor	Conditions/focus	Findings
Uptake, Translocation, Accumulation, Transformation, and Generational Transmission of Nanoparticles in Plants (Shukla et al. 2016)	Review paper	Reviews the current scenario of pathways, mechanisms, and patterns of uptake, translocation, accumulation, transformation, and generational transmission of NPs in plants	NPs can pass through multiple generations of the plants
Trans-generational impact of cerium oxide nanoparticles on tomato plants (Wang et al. 2013)	Tomato/CeO_2/trans-generational effect	CeO_2 NPs (10 mg/L) exposed to tomato through their life cycle; effect on seed quality and development of next-generation seedlings (parameters: biomass, transpiration rate, and reactive oxygen species content)	The next-generation seedlings were smaller and weaker and have smaller biomass, lower water transpiration, and higher reactive oxygen species content and accumulated a higher amount of ceria
Uptake, Translocation, and Transmission of Carbon Nanomaterials in Rice Plants (Lin et al. 2009)	Carbon nanomaterials/rice/ 20, 40, 80, 400, 800 mg/L/ trans-generational effect	To investigate the generational transmission of nanomaterials C70 in rice seeds, to explore trans-generational impacts, to develop seeds from the C70-treated plants	Dynamic uptake, dispersion, and change of fullerene C70 in rice plants; transmission of C70 to the descendants through seeds
Multigenerational exposure to cerium oxide nanoparticles: Physiological and biochemical analysis reveals transmissible changes in rapid cycling *Brassica rapa* (Ma et al. 2016)	*Brassica rapa*/ CeO_2/0–1000 mg/L/ multigenerational effect CeO_2	To assess physiological and biochemical consequences of multigenerational (three) CeO_2 NPs	The second and third generation displayed slower plant growth and smaller biomass; the numbers of seeds produced reduced in the third-generation plant by over 50% plants contained higher concentrations of hydrogen peroxide in their tissues
Investigating the long-term effect of nanoparticles on the growth of *Raphanus sativus* plants: a trans-generational study (Singh and Kumar 2017)	*Raphanus sativus/* ZnO and CuO NPs/ 10, 100, and 1000 mg/kg/trans-generational effect	Trans-generational impact on radish plants due to exposure of CuO and ZnO NPs as a single compound and as a binary mixture	The treated second-generation seeds had smaller seed weight. The second-generation have accumulated Cu and Zn from parent plants; the effect of toxic interaction between CuO and ZnO on plant growth was antagonistic in nature

aggregation properties) and some are soil-based (pore water chemistry, rhizosphere chemistry, microbiota of soil). The change in NP characteristics in the root environment of soil and effect of soil properties on the change in NP characteristics are some important data gaps and seek immediate attention. In addition to this, different types of NPs (carbon-based, metal-based, metal oxide-based) and plant (monocot and dicots) have different uptake and bioaccumulation potential. The NPs also have long-term and multiple generation effects on edible plants with effect on progenies. Table 9.3 summarizes the major data gaps identified for understanding NP uptake in edible plants.

Despite the rapid progress in the area of NPs and plant in the past decade, still, we are in the initial stage of our understanding. Numerous questions, important to scientific and public communities, need to be investigated. Through this work, we tried to investigate the soil-nanoparticle-plant nexus for understanding uptake in edible plants. For this, we reviewed the literature from the last decade and summarized their findings in this study. The NP properties and soil properties are two major factors playing an important role in internal uptake and bioaccumulation in edible plants. Internal uptake of NPs in environmentally relevant condition and understanding the effect of NP composition, size, mobility, and dissolution state on uptake kinetics still lack attention. Previous work indicated that internal uptake is NP- and plant-dependent, yet some questions like why some plants have more/less uptake capability, uptake mechanism for trans-generational studies, and behavior in the presence of a mixture of NPs are still unanswered. The answer to these unanswered questions has direct implications toward food safety. In the end, all these data will be important to the scientific community for prioritizing NPs and plant species with higher accumulation capacities.

Nanotechnology in the agricultural sector is anticipated to become a driving economic force in the near future. Long-term and short-term exposures of NPs can have a negative effect on plant's health. Some metal and metal oxide NPs can have substantial negative effects at cellular levels as well. The present paper documents various factors affecting uptake of NPs in plants. In addition to these various aspects, NP-related properties effecting phytotoxicity should be documented before promoting the application of nanotechnology (Yang et al. 2017). Unavoidable use of pesticides in the agriculture sector has increased exponentially due to increase in population and growing food needs. In this case, food safety is a growing concern among the scientific community. Nano-encapsulation of chemicals used in agrochemicals is relatively new and in the very early stage of development. This technology aims to reduce the indiscriminate use of agrochemicals and increase crop productivity and food safety (Nuruzzaman et al. 2016). In addition to this, nanotechnology has also served as a source of nutrient to the plants in the form of nanofertilizers as well. Nanofertilizers are considered to boost stress tolerance and nutritional quality (Morales-Díaz et al. 2017). However, detailed studies on the effect of these nanofertilizers on plant health, toxicity to organisms, biodiversity, etc. must also be studied. These are some of the limitations of the present work and need detailed understanding in the future. In addition to this, studies on understanding NP characteristics in root environment; changes in NP properties like size,

Table 9.3 Summary of identified data gaps and recommended future work

Parameters	Identified data gaps	Recommended future work
Size of nanoparticles in soil	Effect of factors like electrolyte concentration, ion types (monovalent, divalent ions, and mixture), ionic strength of soil, humic acid content, the texture of the soil, soil type, and concentration on the size of NPs in irrigation water and soil need to be understood	Characterize NPs in the root environment
		Study changes in NP properties like size, charge, and shape during their transport in agricultural soil
The mobility of NPs in soil	The mobility of NPs in soil (applied as irrigation water or sludge) under various governing factors like soil pH, organic matter content, soil texture, and ionic strength needs to be understood	Study effect of environmental factors on NP behavior in agriculture soil
	Effect of different types of soil (clay, sand, silt, and humus content) on mobility as it affects soil pH, which in turn governs mobility of NPs in the soil, needs to be understood	Study fate of NPs in irrigation water and pore water
	Other factors like the effect of light, temperature, soil humidity, and presence of soil microbiota can also affect NP mobility in the environment and should be taken into consideration	Study fate and transport of NPs in soil column with and without plants (it can aid in understanding the effect of root environment on size, mobility, dissolution of NPs)
	The mobility of NPs in the presence of a mixture of other NPs should also be taken into consideration	Study effect of pore water chemistry, rhizosphere chemistry, and microbiota of soil on NP uptake in plants
	Mobility under dynamic flow conditions needs to be explored	
Aggregation of pore water and root environment	The pore water chemistry needs to be properly understood	
	Another important factor affecting aggregation properties of NPs is bacteria and fungi present on root surface which needs more research	
	Aggregation properties of NPs during transport in soil under natural conditions need research	
Change in surface charge in pore water and root environment	Quantification of different properties affecting the surface charge of NPs needs to be understood	

(continued)

Table 9.3 (continued)

Parameters	Identified data gaps	Recommended future work
	Change in surface charge of NPs under different soil-based properties need to be understood	
	Effect of surface charge on the bioavailability of NPs in plants across different soil types, concentration ranges, and timeframes needs to be understood	
Effect of type of nanoparticle on the uptake in edible plants	Uptake is dependent on NP type (metal, metal oxide, carbon nanotubes, quantum dots), and thus it is necessary to understand the fate and transport of these NPs	Use different NPs in uptake studies and understand impacts
	Information on uptake and accumulation potential of NPs in edible plants in the presence of other contaminants (e.g., other NPs) is needed	
Type of plant on NP uptake	Accurate and precise uptake mechanism of NP through monocot and dicot roots in soil media needs to be understood	Use different plant types (monocot, dicot), NPs (size, surface charge, shape, etc.), and soil (pH, organic matter, temperature, texture, etc.), and study their effects on uptake quantification and mechanism
Mechanism of NP uptake in plants	The mechanism of NP uptake in plants is still not very well understood	Use advanced methodologies for obtaining more precise information and for conducting accurate characterization of NPs in edible parts of plants (it may help in the quantification of NPs in edible parts of the plants)
	Understanding of various factors governing the movement of NPs in plant system is not clear	Conduct study to investigate the effect of NPs on cellular and genetic level
	Effect on NP-related properties like size, surface charge, aggregation, and mobility on their movement in xylem and phloem is not studied	Conduct study to obtain information on reactions and processes responsible for the biotransformation of NPs in plants
	The dissolution of ions from NPs (outside the plant, in soil, or inside the plant, after uptake) needs clarification	
	The change in uptake of NPs in the presence of other NPs in a plant environment is lacking from the literature and needs attention	

(continued)

Table 9.3 (continued)

Parameters	Identified data gaps	Recommended future work
Multiple generational effects on NPs in plants	Studies on the transfer of NPs and ions to the multiple generations of the plants and impact on agriculture production is missing	Study the effect of single and mixture of NPs on next and multiple generations of plants
	Life cycle assessment and long-term effect of NPs in the environment is required for understanding risk	Study accumulation and biotransformation of NPs during multiple generational transfers in plants

charge, and shape during their transport in agricultural soil; and fate in irrigation water and pore water are needed. In addition to this, studies on uptake quantification in edible parts of plants, the effect of NPs on cellular and genetic levels, processes responsible for the biotransformation of NPs in plants, and the effect of single and a mixture of NPs on next and multiple generations of plants need immediate attention.

Exposure of NPs in agriculture soil has raised concerns over food safety. An understanding of the factors involved in uptake of NPs in edible plants can help in minimizing risk, and the scientific community can use this information to prioritize NPs and plant species with higher accumulation capacities. The irrigation and sludge application ultimately leads to slow accumulation of NPs in the soil. Plant roots are the only way for the entry of these NPs in the edible parts of the plants. In this work, we have focused on the various NP-based, soil-based, and root-based factors which can possibly play an important role in the movement of NPs inside the plants.

Acknowledgments The authors would like to thank the Indian Institute of Technology (IIT Delhi, India) and Council of Scientific and Industrial Research (CSIR, India) for their help in conducting this study.

References

Al-Salim N, Barraclough E, Burgess E et al (2011) Quantum dot transport in soil, plants, and insects. Sci Total Environ 409:3237–3248. https://doi.org/10.1016/j.scitotenv.2011.05.017

Badri DV, Vivanco JM (2009) Regulation and function of root exudates. Plant Cell Environ 32:666–681. https://doi.org/10.1111/j.1365-3040.2009.01926.x

Baruah S, Dutta J (2009) Nanotechnology applications in pollution sensing and degradation in agriculture: a review. Environ Chem Lett 7:191–204. https://doi.org/10.1007/s10311-009-0228-8

Birbaum K, Brogioli R, Schellenberg M et al (2010) No evidence for cerium dioxide nanoparticle translocation in maize plants. Environ Sci Technol 44:8718–8723. https://doi.org/10.1021/es101685f

Bour A, Mouchet F, Silvestre J et al (2015) Environmentally relevant approaches to assess nanoparticles ecotoxicity: a review. J Hazard Mater 283C:764–777. https://doi.org/10.1016/j.jhazmat.2014.10.021

Bystrzejewska-Piotrowska G, Golimowski J, Urban PL (2009) Nanoparticles: their potential toxicity, waste and environmental management. Waste Manag 29:2587–2595. https://doi.org/10.1016/j.wasman.2009.04.001

Chen G, Liu X, Su C (2012) Distinct effects of humic acid on transport and retention of TiO_2 rutile nanoparticles in saturated sand columns. Environ Sci Technol 46:7142–7150. https://doi.org/10.1021/es204010g

Cifuentes Z, Custardoy L, de la Fuente JM et al (2010) Absorption and translocation to the aerial part of magnetic carbon-coated nanoparticles through the root of different crop plants. J Nanobiotechnol 8:26. https://doi.org/10.1186/1477-3155-8-26

Conway JR, Adeleye AS, Gardea-Torresdey J, Keller AA (2015) Aggregation, dissolution, and transformation of copper nanoparticles in natural waters. Environ Sci Technol 49:2749–2756. https://doi.org/10.1021/es504918q

Cornelis G, Hund-Rinke K, Kuhlbusch T et al (2014) Fate and bioavailability of engineered nanoparticles in soils: a review. Crit Rev Environ Sci Technol 44:2720–2764. https://doi.org/10.1080/10643389.2013.829767

Cox A, Venkatachalam P, Sahi S, Sharma N (2016) Silver and titanium dioxide nanoparticle toxicity in plants: a review of current research. Plant Physiol Biochem 107:147–163. https://doi.org/10.1016/j.plaphy.2016.05.022

Dev A, Srivastava AK, Karmakar S (2017) Uptake and toxicity of Nanomaterials in plants. Springer, Cham, pp 169–204

Dimkpa CO, McLean JE, Latta DE et al (2012) CuO and ZnO nanoparticles: phytotoxicity, metal speciation, and induction of oxidative stress in sand-grown wheat. J Nanopart Res 14:1125. https://doi.org/10.1007/s11051-012-1125-9

Dimkpa CO, McLean JE, Martineau N et al (2013) Silver nanoparticles disrupt wheat (*Triticum aestivum* L.) growth in a sand matrix. Environ Sci Technol 47:1082–1090. https://doi.org/10.1021/es302973y

Dinesh R, Anandaraj M, Srinivasan V, Hamza S (2012) Engineered nanoparticles in the soil and their potential implications to microbial activity. Geoderma 173–174:19–27. https://doi.org/10.1016/j.geoderma.2011.12.018

Ebbs SD, Bradfield SJ, Kumar P et al (2016a) Accumulation of zinc, copper, or cerium in carrot (Daucus carota) exposed to metal oxide nanoparticles and metal ions. Environ Sci Nano 3:114–126. https://doi.org/10.1039/C5EN00161G

Ebbs SD, Bradfield SJ, Kumar P et al (2016b) Projected dietary intake of zinc, copper, and cerium from consumption of carrot (Daucus carota) exposed to metal oxide nanoparticles or metal ions. Front Plant Sci 7:188. https://doi.org/10.3389/fpls.2016.00188

El-Temsah YS, Joner EJ (2012) Impact of Fe and Ag nanoparticles on seed germination and differences in bioavailability during exposure in aqueous suspension and soil. Environ Toxicol 27:42–49. https://doi.org/10.1002/tox.20610

Elzey S, Grassian VH (2010) Agglomeration, isolation and dissolution of commercially manufactured silver nanoparticles in aqueous environments. J Nanopart Res 12:1945–1958. https://doi.org/10.1007/s11051-009-9783-y

Fang J, Shan X, Wen B et al (2009) Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. Environ Pollut 157:1101–1109. https://doi.org/10.1016/j.envpol.2008.11.006

Garner KL, Keller AA (2014) Emerging patterns for engineered nanomaterials in the environment: a review of fate and toxicity studies. J Nanopart Res 16:2503. https://doi.org/10.1007/s11051-014-2503-2

Hedberg J, Oromieh AG, Kleja DB, Wallinder IO (2015) Sorption and dissolution of bare and coated silver nanoparticles in soil suspensions – influence of soil and particle characteristics. J Environ Sci Health A Tox Hazard Subst Environ Eng 50:891–900. https://doi.org/10.1080/10934529.2015.1030271

Hegde K, Brar SK, Verma M, Surampalli RY (2016) Current understandings of toxicity, risks and regulations of engineered nanoparticles with respect to environmental microorganisms. Nanotechnol Environ Eng 1:5. https://doi.org/10.1007/s41204-016-0005-4

Hu Y (2010) High efficiency transport of quantum dots into plant roots with the aid of silwet L-77. Plant Physiol Biochem 48:703–709. https://doi.org/10.1016/J.PLAPHY.2010.04.001

Jacob DL, Borchardt JD, Navaratnam L et al (2013) Uptake and translocation of Ti from nanoparticles in crops and wetland plants. Int J Phytoremediation 15:142–153. https://doi.org/10.1080/15226514.2012.683209

Jośko I, Oleszczuk P, Skwarek E (2017) Toxicity of combined mixtures of nanoparticles to plants. J Hazard Mater 331:200–209. https://doi.org/10.1016/j.jhazmat.2017.02.028

Judy JD, Unrine JM, Rao W et al (2012) Bioavailability of gold Nanomaterials to plants: importance of particle size and surface coating. Environ Sci Technol 46:8467–8474. https://doi.org/10.1021/es3019397

Keller AA, Wang H, Zhou D et al (2010) Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. Environ Sci Technol 44:1962–1967. https://doi.org/10.1021/es902987d

Kittler S, Greulich C, Diendorf J et al (2010) Toxicity of silver nanoparticles increases during storage because of slow dissolution under release of silver ions. Chem Mater 22:4548–4554. https://doi.org/10.1021/cm100023p

Larue C, Laurette J, Herlin-Boime N et al (2012) Accumulation, translocation and impact of TiO2 nanoparticles in wheat (Triticum aestivum spp.): influence of diameter and crystal phase. Sci Total Environ 431:197–208. https://doi.org/10.1016/j.scitotenv.2012.04.073

Lee J-Y, Lu H (2011) Plasmodesmata: the battleground against intruders. Trends Plant Sci 16:201–210. https://doi.org/10.1016/j.tplants.2011.01.004

Lee W-M, An Y-J, Yoon H, Kweon H-S (2008) Toxicity and bioavailability of copper nanoparticles to the terrestrial plants mung bean (Phaseolus radiatus) and wheat (Triticum aestivum): plant agar test for water-insoluble nanoparticles. Environ Toxicol Chem 27:1915–1921

Lee WM, Kwak JI, An YJ (2012) Effect of silver nanoparticles in crop plants Phaseolus radiatus and Sorghum bicolor: media effect on phytotoxicity. Chemosphere 86:491–499. https://doi.org/10.1016/j.chemosphere.2011.10.013

Li X, Lenhart JJ (2012) Aggregation and dissolution of silver nanoparticles in natural surface water. Environ Sci Technol 46:5378–5386. https://doi.org/10.1021/es204531y

Lin S-W, Chen D-H (2009) Synthesis of water-soluble blue Photoluminescent silicon Nanocrystals with oxide surface passivation. Small 5:72–76. https://doi.org/10.1002/smll.200800677

Lin D, Xing B (2008) Root uptake and phytotoxicity of ZnO nanoparticles. Environ Sci Technol 42:5580–5585. https://doi.org/10.1021/es800422x

Lin S, Reppert J, Hu Q et al (2009) Uptake, translocation, and transmission of carbon nanomaterials in rice plants. Small 5:1128–1132. https://doi.org/10.1002/smll.200801556

Ma X, Quah B (2016) Effects of surface charge on the fate and Phytotoxicity of gold nanoparticles to Phaseolus vulgaris. J Food Chem Nanotechnol. https://doi.org/10.17756/jfcn.2016-011

Ma X, Geiser-Lee J, Deng Y, Kolmakov A (2010a) Interactions between engineered nanoparticles (ENPs) and plants: phytotoxicity, uptake and accumulation. Sci Total Environ 408:3053–3061. https://doi.org/10.1016/j.scitotenv.2010.03.031

Ma X, Geisler-Lee J, Geiser-Lee J et al (2010b) Interactions between engineered nanoparticles (ENPs) and plants: phytotoxicity, uptake and accumulation. Sci Total Environ 408:3053–3061. https://doi.org/10.1016/j.scitotenv.2010.03.031

Ma Y, Kuang L, He X et al (2010c) Effects of rare earth oxide nanoparticles on root elongation of plants. Chemosphere 78:273–279. https://doi.org/10.1016/j.chemosphere.2009.10.050

Ma R, Levard C, Judy JD et al (2014) Fate of zinc oxide and silver nanoparticles in a pilot wastewater treatment plant and in processed biosolids. Environ Sci Technol 48:104–112. https://doi.org/10.1021/es403646x

Ma X, Wang Q, Rossi L et al (2016) Multigenerational exposure to cerium oxide nanoparticles: physiological and biochemical analysis reveals transmissible changes in rapid cycling Brassica rapa. NanoImpact 1:46–54. https://doi.org/10.1016/j.impact.2016.04.001

Martinoia E, Baetz U (2014) Root exudates: the hidden part of plant defense. Trends Plant Sci 19:90–98. https://doi.org/10.1016/J.TPLANTS.2013.11.006

Maurer-Jones MA, Gunsolus IL, Murphy CJ, Haynes CL (2013) Toxicity of engineered nanoparticles in the environment. Anal Chem 85:3036–3049. https://doi.org/10.1021/ac303636s

Milewska-Hendel A, Zubko M, Karcz J et al (2017) Fate of neutral-charged gold nanoparticles in the roots of the Hordeum vulgare L. cultivar karat. Sci Rep 7:3014. https://doi.org/10.1038/s41598-017-02965-w

Miralles P, Church TL, Harris AT (2012) Toxicity, uptake, and translocation of engineered Nanomaterials in vascular plants. Environ Sci Technol 46:9224–9239. https://doi.org/10.1021/es202995d

Mishra S, Keswani C, Abhilash PC et al (2017) Integrated approach of Agri-nanotechnology: challenges and future trends. Front Plant Sci 8:471. https://doi.org/10.3389/fpls.2017.00471

Mohd Omar F, Abdul Aziz H, Stoll S (2014) Aggregation and disaggregation of ZnO nanoparticles: influence of pH and adsorption of Suwannee River humic acid. Sci Total Environ 468–469:195–201. https://doi.org/10.1016/j.scitotenv.2013.08.044

Monreal CM, DeRosa M, Mallubhotla SC et al (2016) Nanotechnologies for increasing the crop use efficiency of fertilizer-micronutrients. Biol Fertil Soils 52:423–437. https://doi.org/10.1007/s00374-015-1073-5

Morales-Díaz AB, Ortega-Ortíz H, Juárez-Maldonado A et al (2017) Application of nanoelements in plant nutrition and its impact in ecosystems. Adv Nat Sci Nanosci Nanotechnol 8:13001. https://doi.org/10.1088/2043-6254/8/1/013001

Nair R, Varghese SH, Nair BG et al (2010) Nanoparticulate material delivery to plants. Plant Sci 179:154–163. https://doi.org/10.1016/j.plantsci.2010.04.012

Nuruzzaman M, Rahman MM, Liu Y, Naidu R (2016) Nanoencapsulation, Nano-guard for pesticides: a new window for safe application. J Agric Food Chem 64:1447–1483. https://doi.org/10.1021/acs.jafc.5b05214

Pan B, Xing B (2012) Applications and implications of manufactured nanoparticles in soils: a review. Eur J Soil Sci 63:437–456. https://doi.org/10.1111/j.1365-2389.2012.01475.x

Pappas S, Turaga U, Kumar N et al (2017) Effect of concentration of silver nanoparticles on the uptake of silver from silver nanoparticles in soil. Int J Environ Agric Res 3:80–90. https://doi.org/10.25125/agriculture-journal-IJOEAR-MAY-2017-12

Pavlaki MD, Pereira R, Loureiro S, Soares AMVM (2011) Effects of binary mixtures on the life traits of Daphnia magna. Ecotoxicol Environ Saf 74:99–110. https://doi.org/10.1016/j.ecoenv.2010.07.010

Pelley AJ, Tufenkji N (2008) Effect of particle size and natural organic matter on the migration of nano- and microscale latex particles in saturated porous media. J Colloid Interface Sci 321:74–83. https://doi.org/10.1016/j.jcis.2008.01.046

Pérez-de-Luque A, Rubiales D (2009) Nanotechnology for parasitic plant control. Pest Manag Sci 65:540–545. https://doi.org/10.1002/ps.1732

Poma A, Colafarina S, Fontecchio G, Chichiriccò G (2014) Transgenerational effects of NMs. Springer, Dordrecht, pp 235–254

Qi Z, Zhang L, Chen W (2014) Transport of graphene oxide nanoparticles in saturated sandy soil. Environ Sci Process Impacts 16:2268–2277. https://doi.org/10.1039/c4em00063c

Rai M, Ingle A (2012) Role of nanotechnology in agriculture with special reference to management of insect pests. Appl Microbiol Biotechnol 94:287–293. https://doi.org/10.1007/s00253-012-3969-4

Raliya R, Nair R, Chavalmane S et al (2015) Mechanistic evaluation of translocation and physiological impact of titanium dioxide and zinc oxide nanoparticles on the tomato (Solanum lycopersicum L.) plant. Metallomics 7:1584–1594. https://doi.org/10.1039/C5MT00168D

Ram P, Vivek K, Kumar SP (2014) Nanotechnology in sustainable agriculture: present concerns and future aspects. Afr J Biotechnol 13:705–713. https://doi.org/10.5897/AJBX2013.13554

Read DS, Matzke M, Gweon HS et al (2016) Soil pH effects on the interactions between dissolved zinc, non-nano- and nano-ZnO with soil bacterial communities. Environ Sci Pollut Res 23:4120–4128. https://doi.org/10.1007/s11356-015-4538-z

Reidy B, Haase A, Luch A et al (2013) Mechanisms of silver nanoparticle release, transformation and toxicity: a critical review of current knowledge and recommendations for future studies and applications. Materials (Basel) 6:2295–2350. https://doi.org/10.3390/ma6062295

Rico CM, Majumdar S, Duarte-Gardea M et al (2011) Interaction of nanoparticles with edible plants and their possible implications in the food chain. J Agric Food Chem 59:3485–3498. https://doi.org/10.1021/jf104517j

Rizwan M, Ali S, Qayyum MF et al (2017) Effect of metal and metal oxide nanoparticles on growth and physiology of globally important food crops: a critical review. J Hazard Mater 322:2–16. https://doi.org/10.1016/j.jhazmat.2016.05.061

Ruffini Castiglione M, Giorgetti L, Geri C, Cremonini R (2011) The effects of nano-TiO2 on seed germination, development and mitosis of root tip cells of Vicia narbonensis L. and Zea mays L. J Nanopart Res 13:2443–2449. https://doi.org/10.1007/s11051-010-0135-8

Sabo-Attwood T, Unrine JM, Stone JW et al (2012) Uptake, distribution and toxicity of gold nanoparticles in tobacco (Nicotiana xanthi) seedlings. Nanotoxicology 6:353–360. https://doi.org/10.3109/17435390.2011.579631

Sajid M, Ilyas M, Basheer C et al (2015) Impact of nanoparticles on human and environment: review of toxicity factors, exposures, control strategies, and future prospects. Environ Sci Pollut Res 22:4122–4143. https://doi.org/10.1007/s11356-014-3994-1

Saleh N, Kim H-J, Phenrat T et al (2008) Ionic strength and composition affect the mobility of surface-modified Fe ^{0} nanoparticles in water-saturated sand columns. Environ Sci Technol 42:3349–3355. https://doi.org/10.1021/es071936b

Schwab F, Zhai G, Kern M et al (2015) Barriers, pathways and processes for uptake, translocation and accumulation of nanomaterials in plants ? Crit Rev Nanotoxicol:1–22. https://doi.org/10.3109/17435390.2015.1048326

Schwabe F, Tanner S, Schulin R et al (2015) Dissolved cerium contributes to uptake of Ce in the presence of differently sized CeO_2 -nanoparticles by three crop plants. Metallomics 7:466–477. https://doi.org/10.1039/C4MT00343H

Serag MF, Kaji N, Gaillard C et al (2011) Trafficking and subcellular localization of multiwalled carbon nanotubes in plant cells. ACS Nano 5:493–499. https://doi.org/10.1021/nn102344t

Shih Y, Zhuang C, Peng Y-H et al (2012) The effect of inorganic ions on the aggregation kinetics of lab-made TiO2 nanoparticles in water. Sci Total Environ 435–436:446–452. https://doi.org/10.1016/j.scitotenv.2012.06.076

Shin S, Song I, Um S (2015) Role of physicochemical properties in nanoparticle toxicity. Nano 5:1351–1365. https://doi.org/10.3390/nano5031351

Shukla PK, Misra P, Kole C (2016) Uptake, translocation, accumulation, transformation, and generational transmission of nanoparticles in plants. Plant nanotechnology. Springer, Cham, pp 183–218

Siddiqi KS, Husen A (2017) Plant response to engineered metal oxide nanoparticles. Nanoscale Res Lett 12:92. https://doi.org/10.1186/s11671-017-1861-y

Singh D, Kumar A (2016) Impact of irrigation using water containing CuO and ZnO nanoparticles on spinach oleracea grown in soil media. Bull Environ Contam Toxicol. https://doi.org/10.1007/s00128-016-1872-x

Singh D, Kumar A (2017) Investigating long-term effect of nanoparticles on growth of Raphanus sativus plants: a trans-generational study. Ecotoxicology:1–9. https://doi.org/10.1007/s10646-017-1867-3

Song U, Jun H, Waldman B et al (2013) Functional analyses of nanoparticle toxicity: a comparative study of the effects of TiO2 and Ag on tomatoes (Lycopersicon esculentum). Ecotoxicol Environ Saf 93:60–67. https://doi.org/10.1016/j.ecoenv.2013.03.033

Sun D, Hussain HI, Yi Z et al (2014) Uptake and cellular distribution, in four plant species, of fluorescently labeled mesoporous silica nanoparticles. Plant Cell Rep 33:1389–1402. https://doi.org/10.1007/s00299-014-1624-5

Tourinho PS, van Gestel CAM, Lofts S et al (2012) Metal-based nanoparticles in soil: fate, behavior, and effects on soil invertebrates. Environ Toxicol Chem 31:1679–1692. https://doi.org/10.1002/etc.1880

Vacheron J, Desbrosses G, Bouffaud M-L et al (2013) Plant growth-promoting rhizobacteria and root system functioning. Front Plant Sci 4:356. https://doi.org/10.3389/fpls.2013.00356

Vittori Antisari L, Carbone S, Gatti A et al (2015) Uptake and translocation of metals and nutrients in tomato grown in soil polluted with metal oxide (CeO2, Fe3O4, SnO2, TiO2) or metallic (Ag, Co, Ni) engineered nanoparticles. Environ Sci Pollut Res 22:1841–1853. https://doi.org/10.1007/s11356-014-3509-0

Waalewijn-Kool PL, Diez Ortiz M, van Straalen NM, van Gestel CAM (2013) Sorption, dissolution and pH determine the long-term equilibration and toxicity of coated and uncoated ZnO nanoparticles in soil. Environ Pollut 178:59–64. https://doi.org/10.1016/j.envpol.2013.03.003

Wang Y, Li Y, Pennell KD (2008) Influence of electrolyte species and concentration on the aggregation and transport of fullerene nanoparticles in Quartz Sands. Environ Toxicol Chem 27:1860. https://doi.org/10.1897/08-039.1

Wang Q, Ebbs SD, Chen Y, Ma X (2013) Trans-generational impact of cerium oxide nanoparticles on tomato plants. Metallomics 5:753. https://doi.org/10.1039/c3mt00033h

Wang P, Lombi E, Sun S et al (2017) Characterizing the uptake, accumulation and toxicity of silver sulfide nanoparticles in plants. Environ Sci Nano 4:448–460. https://doi.org/10.1039/C6EN00489J

Winkel-Shirley B, McCully M, Canny M et al (2001) Flavonoid biosynthesis. A Colorful model for genetics, biochemistry, cell biology, and biotechnology. Plant Physiol 126:485–493. https://doi.org/10.1104/pp.126.2.485

Yang J, Cao W, Rui Y (2017) Interactions between nanoparticles and plants: phytotoxicity and defense mechanisms. J Plant Interact 12:158–169. https://doi.org/10.1080/17429145.2017.1310944

Yu R, Wu J, Liu M et al (2016) Toxicity of binary mixtures of metal oxide nanoparticles to Nitrosomonas europaea. Chemosphere 153:187–197. https://doi.org/10.1016/j.chemosphere.2016.03.065

Zhang Z, He X, Zhang H et al (2011) Uptake and distribution of ceria nanoparticles in cucumber plants. Metallomics 3:816–822. https://doi.org/10.1039/c1mt00049g

Zhang P, Ma Y, Zhang Z et al (2012) Biotransformation of ceria nanoparticles in cucumber plants. ACS Nano 6:9943–9950. https://doi.org/10.1021/nn303543n

Zhao L, Peralta-Videa JR, Ren M et al (2012a) Transport of Zn in a sandy loam soil treated with ZnO NPs and uptake by corn plants: Electron microprobe and confocal microscopy studies. Chem Eng J 184:1–8

Zhao L, Peralta-Videa JR, Varela-Ramirez A et al (2012b) Effect of surface coating and organic matter on the uptake of CeO2 NPs by corn plants grown in soil: insight into the uptake mechanism. J Hazard Mater 225–226:131–138. https://doi.org/10.1016/j.jhazmat.2012.05.008

Zhao L, Sun Y, Hernandez-Viezcas JA et al (2013) Influence of CeO $_2$ and ZnO nanoparticles on cucumber physiological markers and bioaccumulation of Ce and Zn: a life cycle study. J Agric Food Chem 61:11945–11951. https://doi.org/10.1021/jf404328e

Zhu Z-J, Wang H, Yan B et al (2012) Effect of surface charge on the uptake and distribution of gold nanoparticles in four plant species. Environ Sci Technol 46:12391–12398. https://doi.org/10.1021/es301977w

Chapter 10
Semiconductor Nanomaterials for Gas Sensor Applications

Hassan Shokry Hassan and Marwa Farouk Elkady

Contents

10.1 Introduction and Historical Overview 307
10.2 Review of Solid-State Gas Sensors 309
  10.2.1 Catalytic Sensors 309
  10.2.2 Pellistor-Type Catalytic Gas Sensor 311
  10.2.3 Thermoelectric Gas Sensor 312
  10.2.4 Thermal Conductivity Gas Sensor 313
  10.2.5 Electrochemical Gas Sensors 314
  10.2.6 Amperometric Gas Sensor 315
  10.2.7 Potentiometric Gas Sensors 317
  10.2.8 Optical Gas Sensors 317
  10.2.9 Infrared Gas Sensor 318
  10.2.10 Acoustic Wave Gas Sensors 319
  10.2.11 SAW-Based Gas Sensors 321
  10.2.12 Semiconductor Gas Sensors 322
10.3 Applications of Gas Sensors 340
  10.3.1 Environmental Applications 341
  10.3.2 Automotive Applications 341
  10.3.3 Biomedical Applications 342
  10.3.4 Health-Care Application 342
  10.3.5 Miscellaneous Applications 344
  10.3.6 New Opportunities 344
10.4 Conclusions 345
References 346

H. S. Hassan
Electronic Materials Researches Department, Advanced Technology and New Materials Researches Institute, City of Scientific Researches and Technological Applications, New Borg El-Arab City, Alexandria, Egypt

Physics Department, Faculty of Science, Aljouf University, Aljouf, Saudi Arabia

M. F. Elkady (✉)
Chemical and Petrochemical Engineering Department, Egypt-Japan University for Science and Technology, New Borg El-Arab City, Alexandria, Egypt

Fabrication Technology Researches Department, Advanced Technology and New Materials and Research Institute, City of Scientific Research and Technological Applications, Alexandria, Egypt

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1_10

Abstract Nanotechnology is the engineering and art of manipulating matter at the nanoscale. The adaptability of physical and chemical properties of metal, semiconductor, noble, and composite nanoparticles renders them as promising materials in the fields ranging from optoelectronics to sensors. These nanoparticles or their self-assemblies are able to distinguish the mixtures of gases, volatile organic compounds, and others. Detection of pollutant, toxic, refining, and combustible gases is significant for framework and process control, safety monitoring, and environmental safeguard. In the last two decades, there have been essential improvements in two key areas that may make this guarantee a reality. First is the improvement of a diversity of excellent performing nanostructured metal oxide semiconductors (MOSs), the most commonly utilized materials for gas sensing. Second are advances in very low power loss reduced heater elements.

Here we review an overview about the principles and the technologies used in solid-state gas sensors. These devices work by measuring a physical property changed by adsorption/desorption processes and chemical reactions on the surface of a sensing element, i.e., a solid-state film of a gas-sensitive material. Some of the most used kinds of solid-state gas sensors are here described jointly with new sensor technologies in progress for commercial exploitation in the future. The analysis of different parameters of metal oxides and the search of criteria, which could be utilized through material chosen for solid-state gas sensor applications, were the main objectives of this chapter. Finally, the future horizons of such semiconductor nanomaterials for gas-sensing applications are also highlighted.

Keywords Gas sensor · Nanomaterials · Metal oxide semiconductor · Conducting polymers · Environmental monitoring · Sensing materials · Sensitivity · Gas sensors applications

Abbreviations

AACVD	Aerosol-assisted chemical vapor deposition
BAW	Bulk acoustic waves
CVD	Chemical vapor deposition
IDT	Interdigitated transducer
MEMS	Micro-electrochemical systems
MHP	Microhotplate
MOSs	Metal oxide semiconductors
NDIR	Nondispersive infrared
PECVD	Plasma-enhanced chemical vapor deposition
PEM	Proton exchange membrane
QCM	Quartz crystal microbalance
QMB	Quartz microbalances
SAW	Surface acoustic wave

VOC	Volatile organic compounds
YSZ	Yttria-stabilized zirconia

10.1 Introduction and Historical Overview

In the last decade, the applications of nanomaterials have received increasingly magnificent attention in the field of nanotechnology, biotechnology, and bioanalytical chemistry. With regard to environmental applications, nanotechnology displays the potential of novel functional materials, procedures, and devices with unique effectiveness toward some contaminants, development of mobility in environmental media, and desired application elasticity.

Over the past six decades, there has been an increasing request for cheap, accurate, portable, and effective gas sensors that can distinguish between very low concentrations of analytes. Typically, gases of interest include NO, CO, CH_4, CO_2, NH_4, SO_2, NO_2, and other hydrocarbons. These gases can be harmful to human health if present outside a specific concentration. Historically, gas sensors were first mostly used in coal mines where exact detection of hazardous gases has to be carried out continually. Readily gas sensors were also beginning to appear in the chemical industry, in environmental pollution sensing units, and in the human health strip. Some other significant applications of gas sensors include the analysis of organic vapors (methanol, toluene, benzene, etc.) for laboratory, industrial safety, diseases diagnosis, and breath analysis for traffic safety (Wang et al. 1995; Mitsubayashi et al. 2004, McEntegart et al. 2000). An electronic nose, based on arrays of gas sensors for testing aroma of food, perfumes and synthetic fragrances, etc., is one of the more recent personifications of gas sensing that has received much interest owing to its enhanced analytical power (Arshak et al. 2004).

Many fields of nanotechnology are based on physical and chemical interactions, including nanoparticles of specific size and shape. Nanoparticles (NPs) played a significant role in absorption/adsorption process of (volatile) organic molecules and gases due to their large specific surface area and high surface energy (Chen et al. 2006a, b). Nanoscale inorganic materials have received significantly more consideration because of their high chemical inertness, non-swelling influence, high purity, and hardness (El Kady et al. 2016). In order to use the nanomaterials as sensors, one has to understand the features of both the installation and interaction technique during the sensing action. In recent years, the interest of scientists and engineers to gas- and liquid-sensitive materials has grown extraordinarily because of the advances in nanotechnology. This attention is fundamentally connected to the promising electronic properties of nanomaterials, their size dependence, and the potential of controlling the material structure by using new experimental methods (El-Aassar et al. 2016). New generations of low-power, low-cost, and portable sensing devices are needed for monitoring of chemistry, medical, agriculture, and manufacturing environments. With the recent progress in nanoscience and nanotechnology, there is an urgent need for adaptable, mechanically durable, and environmentally stable chemical vapor sensors with a high efficiency and low power consumption. Among the major trends in the particle-gas-sensor nanotechnology, the invention of sensor arrays or electronic noses should be listed. Such multi-sensor systems can be fabricated on a single substrate, which can include gas sensors of various types. There are many models of sequential productions of their nanostructured prototypes, which are able to discriminate the mixtures of gases, volatile organic compounds, and odors (Font et al. 2011).

In recent years, great attention has been paid to inorganic nano-sized crystals because of their significant characteristics determined by the high surface areas and quantization of most electronic properties. Nanometer-sized inorganic particles potentially have unparalleled properties because of quantum confinement effects and their large surface area comparative to their volume. The versatility of physical and chemical properties of metal and semiconductor nanoparticles renders them as favorable materials in the fields extending from optoelectronics, sensors, to medicine. Till now, great research attentions have been involved in preparation nanoparticle assemblies because they represent a popular route toward the preparation of advanced functional materials as well as a central concept in nanoscience and nanotechnology (Elkady and Hassan 2015).

It has been known for a long time that electrical impedance of a semiconductor is very sensitive to the presence of defects in its volume or at the surface. At the beginning of the 1950s, Brattain and Bardeen gave the first proof that some semiconductor materials such as Ge change their resistance, depending on the atmosphere they are in contact with (Brattain and Bardeen 1952). Subsequently, Heiland furthermore found that metal oxides such as ZnO alter their semiconducting aspects with a change in the partial pressure of oxygen or other gases in the surrounding atmosphere (Heiland 1957). However, these results were not delicate further. The same properties were reported for SnO_2 with higher stability. These results started further evolution of trade gas sensors.

Chemoresistive gas sensors were inserted for the first time 50 years ago. In 1962, Seiyama used ZnO thin film as a sensing layer and was able to confirm that gas sensing is possible with simple electrical devices (Seiyama and Kato 1962). He used an unpretentious chemoresistive device based on ZnO thin films operating at the temperature of 485 °C. The response of the sensing system to propane was about 100 times higher comparing with the thermal conductivity detector used at that time.

Then, in 1967 Shaver described the detection effects of oxide semiconductors with small additives of noble metals such as Pt, Pd, Ir, and Rh (Shaver 1967). Since that time, the sensitivity and selectivity of semiconductor sensing devices have been developed dramatically, and the search of new sensing materials has been concentrated.

At the beginning of the 1970s, Taguchi fabricated and patented the first chemoresistive gas sensor device for practical applications using tin dioxide (SnO_2) as the sensitive material (Taguchi 1971). Certainly, after investigating many sensitive metal oxides, he found that SnO_2 has many advantage aspects (e.g., higher sensitivity, low operating temperature, and thermal stability).

In the late 1980s, the field of semiconductor gas sensors underwent a considerable development and became one of the most attractive research areas within the sensor society. The request for high-performance gas sensors with high sensitivity and selectivity and faster response with low power consumption and reliability created intense efforts in order to improve novel sensing materials. The quick development of materials chemistry and the more extensive field of materials science have prompted to a dramatic increment in the number of new sensing materials (Seiyama 1988; Yamazoe 1991).

Seiyama probably would not have been able to predict that, half a century after the publication of his fundamental paper, research on gas sensor would consider a significant role in daily life. Certainly, the most recent five decades, due to their simplicity, small size, low cost, and ability to be integrated into electronic devices. Chemical sensors have seen an increase in their application to a variety of fields, including environmental monitoring, industrial emission control, vehicle emission control, domestic security, agricultural, biomedical, etc. (Shimizu and Egashira 1999; Yamazoe 2005).

Several decades after the first published paper on SnO_2 sensors, researchers became the best-understood prototype of oxide-based gas sensors. It was well known that the sensor properties may be changed by modifying the crystal structures, doping, preparation techniques, operation temperatures, etc. (Neri 2015).

Now, the expansion of semiconducting sensing materials is depending on opportunities presented by new nanotechnology. Furthermore, emerging nanotechnologies promise dramatic changes in sensor designs and abilities.

10.2 Review of Solid-State Gas Sensors

Gas sensors can be categorized according to the operation mechanism (semiconductors, flame ionization, photoionization, electrochemical, thermal conductivity, oxidation, light scattering, catalytic photoionization, combustible, colorimetric, infrared or ultraviolet, absorption, etc.). In this section a review on the various kinds of sensors and their principle of operation will be discussed.

10.2.1 Catalytic Sensors

Catalytic sensors have been in use for almost a century to be used in detection of combustible gases. Jonson invented the first catalytic combustion-type sensor in 1923 (Firth et al. 1973) which was used for the detection of methane in mines.

Principle of Operation

Most kinds of metal oxides and their compounds have catalytic property. Combustible gas mixtures do not burn until they get a specific ignition temperature; nevertheless in the presence of a particular chemical process, the gas will begin to burn even at lower temperatures. This process is known as catalytic combustion. Catalytic gas sensor is a gas sensor made on the basis of catalytic principle. A Wheatstone bridge is used to measure the output of catalytic gas sensor. The catalytic gas sensor is divided into two, namely, pellistor type and thermoelectric type. The earliest catalytic gas sensor overview was simply a coil-shaped platinum wire (Fig. 10.1a). This was used to produce an effective heating and a strong signal for a gas sensor; however in spite of the perfect attributes of platinum, it is still a poor catalyst for combustion of hydrocarbon gases. The temperature needed for the sensing of hydrocarbons is between 900 °C and 1000 °C, but at this temperature, the platinum starts to evaporate, and as such resistance of the platinum wire increases.

Another disadvantage with the platinum wire is that at the temperature of 1000 °C, the platinum becomes tender. The solution to this problem is to overcoat the platinum with other metal oxides and then treat the sensor with a catalyst like palladium, platinum, or thoria compounds. Figure 10.1b shows a catalytic bead sensor with the metal oxide coating; the coating makes the sensor more stable, harder, and resistant to shock and vibrations.

Recently, microhotplates have been widely used in gas sensors instead of using platinum coil due to the high power consumption. These kinds of sensors always contain a catalytic surface coated on a hot plate with Pt resistor which heats up the

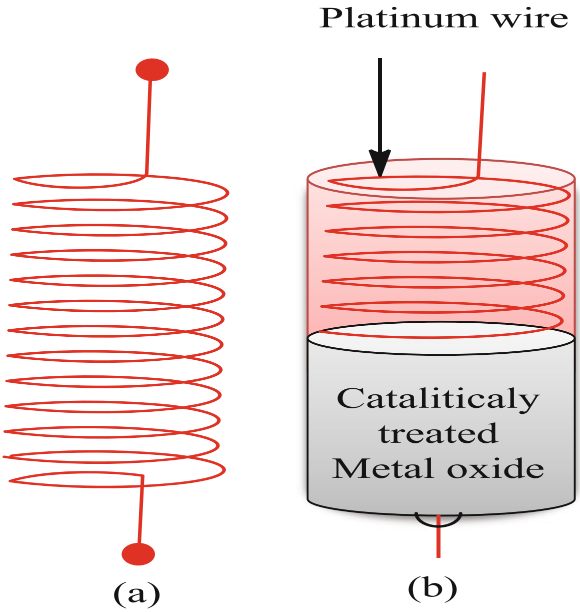


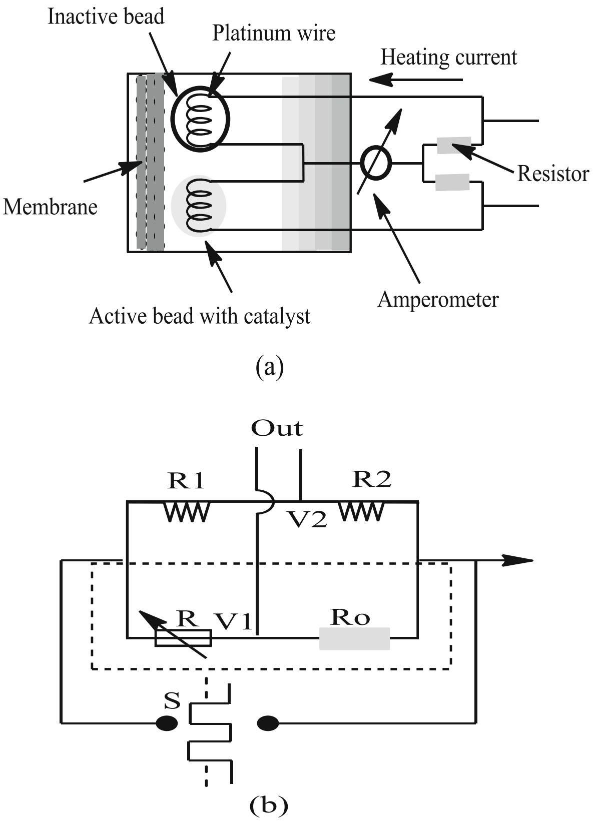
Fig. 10.1 Catalytic sensors. (**a**) Hot-wire sensor, (**b**) catalytic bead sensor

catalyst to a very high temperature at which any flammable gas molecules can ignite. The concentrations of gases can be detected by measuring resistance change of the platinum resistance emerge from increase in temperature. This design was recently developed by Lei Xu et al. in which they design and construct a two-beam microplate for catalytic gas sensors (Karthikeyan et al. 2015). The two-beam microplate was designed using MEMS technology. Their design manifested low power consumption with a 30% power per active area as compared with other microhotplates, and a sensitivity of the sensor to 50% LEL methane was 2.4 mV/ % methane.

10.2.2 Pellistor-Type Catalytic Gas Sensor

A pellistor-type catalytic gas sensor is depicted in Fig. 10.2a consisting of two platinum coils which have two functions. They serve as heater as well as resistance thermometer. It also consists of active and inactive beads. The active bead is activated with catalyst made from a metal like platinum or palladium. The inactive

Fig. 10.2 (**a**) Pellistor-type gas sensor. (**b**) Wheatstone bridge setup for methane gas detection



bead has no catalyst but usually plays as compensating element. A voltage source use for powering the circuit heats up the coils; so the beads are increased to a high temperature from a range of 300 °C to 500 °C depending on the target gas. This causes the gas to ignite and raises the temperature of the detector coil.

This increase in temperature raises the coil resistance and causes an imbalance in the voltage of the Wheatstone bridge which constitutes the detector signal. The output of the sensor is taken across the Wheatstone bridge circuit as shown in Fig. 10.2b. Recent researchers (Xu et al. 2010) enhanced a catalytic combustion-type methane detection sensor with a Pd-Pt catalyst working on pulse voltage mode. The sensor was fabricated by micromachining and sol-gel process on a silicon substrate. The output of the gas sensor is measured by a bridge circuit which consists of a resistive sensing element, microhotplate with a Pd-Pt-Al_2O_3 layer, a variable resistor R, and two fixed resistors R1 and R2.

The pellistor technology has witnessed significant development by using micro-electrochemical systems (MEMS) technology for their fabrication due to the advantage of integration, miniaturization, and reduced power consumption. Catalytic gas combustion gas sensors have been fabricated using thin-film or micromachining technologies. Recently, Lee et al. developed an integrated catalytic combustion H_2 sensor using MEMS technology (Lee et al. 2011). The novelty of their design was that the gas sensors were fabricated with two sensing elements and two reference elements using MEMS technology.

10.2.3 Thermoelectric Gas Sensor

In 1985 McAleer invented the earliest thermoelectric gas sensor for the detection of combustible gas like H_2 gas as reported by Shin et al. (Shin et al. 2003, 2004). Hydrogen detection using thermoelectric sensor is possible by generating an electrical signal based on the catalyzed exothermic oxidation reaction of hydrogen. Thermoelectric gas sensors work on the principle of the Seebeck effect. The Seebeck effect occurs as a result of a temperature change between two points of a conductor or semiconductor material which gives increase to a voltage difference between these two points. Thermoelectric sensors have been manufactured using micromachining techniques. A microelectric gas sensor for the detection of hydrogen and atomic oxygen was reported by Se-Chuk Park et al. using surface micromachining technique for the sensor fabrication (Kim et al. 2009). The sensor senses the gases by measuring the reaction temperature of the catalytic reaction between a novel metal catalyst using Cu-Bi thermopiles. Hydrogen recently reported thermoelectric sensors were used for the detection of volatile organic compounds (VOCs) by the use of SnO_2 thin films. The precept of gas sensing using thermoelectric gas sensors is usually based on gas absorption. Nevertheless this technique usually slows down the response and recovery times. Seung-Il Yoon et al. (Yoon et al. 2009) invented and fabricated a thermoelectric gas sensor based on the principle of gas adsorption instead of gas absorption. The sensor uses an embedded tin oxide catalyst for the detection of hydrogen and NO_x gases. MEMS technology was employed for the sensor fabrication on a Pyrex substrate. To understand the principle of gas adsorption, sensing and reference thermopiles with Bi and Cr pairs were used. A thermopile was used so as to produce an electric potential that is proportionate to the temperature variation between the hot and cold junctions without the need of power consumption while a catalyst film is placed underneath the hot junctions of the thermopile.

A thermoelectric gas sensor for the detection of volatile organic compounds was fabricated and developed by S. Anuradha et al. (Anuradha and Rajanna 2006). The sensor was evaluated for response toward VOC, namely, ethanol, isopropyl alcohol, and hexane, in the temperature range of about 80–160 °C. The sensors developed with and without the metal films were tested for their response to acetone gas. Sensors with chromium metal showed good sensitivity to acetone as low as 28 ppm and were found to be selective toward acetone gas.

10.2.4 Thermal Conductivity Gas Sensor

Gases with thermal conductivities less than air are difficult to sense using this way due to interference of, for example, carbon dioxide and butane. Their principle of operation is based on the measured heat loss from a hotter body to the cold element through thermal conductivity. The first type of thermal conductivity gas sensor is called pellistor-like sensor, and it consists of two inert resistor beads with an implanted thermoresistor. The sensing device is usually located within a gas chamber which contains a reference gas. Comparable to a catalytic gas sensor, a Wheatstone bridge circuit is also utilized whereby the two beads are connected. The principle of the detection mechanism is such that when the resistor is exposed to the target gas mixture, heat is lost which is either higher or lower depending on the thermal conductivity of the target gas with respect to the reference gas. This leads to an increasing or decreasing temperature of the bead and furthermore a difference in its resistance which is measured as an imbalance in the Wheatstone bridge. The second type of sensor doesn't need the use of reference cell because it is made up of a hot and cold element which has a known and a constant temperature variance. The heat is transferred from the hot element to the cold element by means of thermal conductivity of the investigated gas (Yunusa et al. 2014).

Tardy et al. (2004) developed a dynamic thermal conductivity sensor based on the transient response of a SiC microplate for the determination of CO, H_2, and CH_4. Simon and Arndt fabricated a simple micromachined thermal conductivity sensor. Experiments carried out showed good sensor performance predicted by the model. The sensor chips were used to build a hydrogen detector for automotive applications (Simon and Arndt 2002).

Recently, micromachining have been used for hydrogen gas sensor due to miniaturization and reduced power consumption. De-Graaf and Wolffenbuttel (2012) recently developed a thermal conductivity gas sensing which uses MEMS technology for the fabrication of high-sensitivity thermal sensors for hydrogen detection. The analysis showed that the performance of surface-micromachined devices could be better than that of bulk-micromachined devices. It is made up of thermopile temperature sensors which depend upon the reduction in efficient thermal resistance between the sensitive area of the sensor and the substrate by the thermal conductance of the gas in the thin membrane. The heating element is a resistor which is set in the middle of the membrane. A gas chamber is located for the hydrogen sensing.

10.2.5 Electrochemical Gas Sensors

These types of sensors allow gases to diffuse through a porous membrane to an electrode where it is either reduced or oxidized at the electrode. Electrochemical sensors operate by reacting with a target gas and producing an electrical signal that is proportional to the gas concentration. A typical electrochemical gas sensor consists of a sensing electrode or working electrode and a counter electrode which are separated by a thin layer of electrolyte. Before the gas comes in contact with the sensor, it goes through a thin capillary-type opening and then diffuses through a hydrophobic barrier before finally reaching the electrode surface. The function of this membrane is to prevent liquid electrolyte from leaking out and generate enough electrical signal at the sensing electrode. It also consists of a reference electrode whose function is to maintain a stable and constant potential at the sensing electrode due to the continuous electrochemical reactions occurring on the electrode surface. The electrochemical reaction with the target gas generates a flow of current flow between the sensing and counter electrodes. The electrolyte is responsible for carrying the ionic charges across the electrode.

The earliest electrochemical cells were reported by Kohlraush in 1885 and Haber in the early 1900s (Hübert et al. 2011). Since after that a lot of researchers have worked on electrochemical gas sensors for detection of different gases. Currie et al. (1999) developed micromachined thin solid-state electrochemical sensor for simultaneous detection of CO_2, NO_2, and SO_2 gases. Similarly, Sathiyamoorthi et al. (2004) developed an electrochemical sensor for the detection of fluorine and chlorine. In order to improve the sensitivity of the electrochemical gas sensor, Gan and Hu (2011) published a review paper on electrochemical sensors based on graphene materials; due to the fact that nanoscale materials are good candidates for gas-sensing elements due to high surface-to-volume ratio, they have reduced size and reduced power consumption and have been used for the detection of various gases as shown by Lu et al. (2009a, b). However, microelectronic systems (MEMS) have been employed for the design of electrochemical microsensors, and efforts have been made to improve their sensitivity as shown by Zhang et al. (2008).

They explained that improved sensitivity could be attained by coating nanosensors developed from carbon nanotubes with polymers. An electrochemical sensor can be used for measuring carbon monoxide by undergoing a chemical reaction as follows:

$$CO + H_2O \rightarrow CO_2 + 2H + +2e^- \tag{10.1}$$

As shown in Eq. (10.1), oxidation reaction takes place at the sensing electrode, CO_2 diffuses into the air, and the positively charged ions migrate into the electrolyte.

$$O + 4H^+ + 4e^- \rightarrow 2HO \tag{10.2}$$

The oxidation reaction is balanced by a corresponding reduction reaction at the counter electrode as shown in Eq. (10.2). At one electrode, water is consumed, while electrons are generated, and at the other electrode, water is created, while electrons are consumed. The carbon monoxide generated diffuses in the air, and the positively charged hydrogen ions travel down to the electrolyte.

Similarly, for hydrogen the electrochemical reaction is shown in Eq. (10.3). Hydrogen gas diffuses and becomes oxidized at the sensing electrode. This reaction causes a change in the potential of the sensing electrode, and thus reduction of oxygen takes place as shown in Eq. (10.4):

$$H \rightarrow 2H^+ + 2e^- \tag{10.3}$$

$$\tfrac{1}{2}\, O + H^+ + e^- \rightarrow H_2O \tag{10.4}$$

The result of the flow of electrons from anode to the cathode constitutes an electric current that is proportional to the hydrogen gas concentration which obeys Faraday's law:

$$i = Z.F.Q \tag{10.5}$$

where Z is the number of exchanged electrons/molecules, Q is the conversion rate of hydrogen in moles/second, and F is Faraday constant = 96486.7 As/mol. Electrochemical sensors are usually of three types, namely, amperometric, potentiometric, and conductometric, which are discussed below.

10.2.6 Amperometric Gas Sensor

The amperometric sensors work at a constant applied voltage, and the sensor signal is a diffusion-limited current. It usually consists of two electrodes, the working electrode and the counter electrode, and also a reference electrode which are immersed in the electrolyte solution and a potentiostat for maintaining constant voltage as shown in Fig. 10.3.

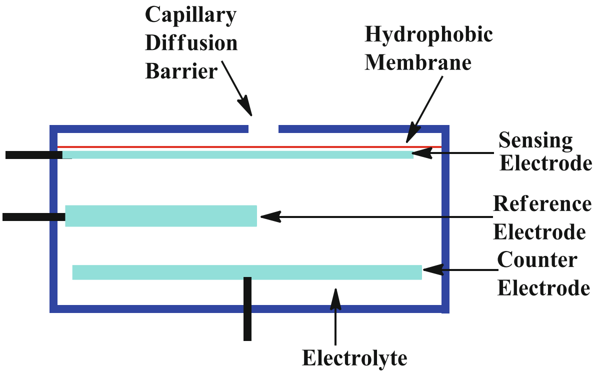


Fig. 10.3 A typical electrochemical gas sensor

Amperometric sensors are usually built using two-electrode configuration, but due to the limits of the concentrations of reactant gas, they are built using a three-electrode scheme. In the three-electrode configuration, the current at the sensing electrode can be measured at a constant potential which gives a genuine thermodynamic potential for all reactions; in this case the reference electrode is not involved in the reaction. However, the current generated as a result of the target gas at the sensing or working electrode is measured as the sensor signal which can then be measured at either a fixed or variable electrode potential.

Amperometric sensors have been used for detecting various gases by changing the type of electrolyte. Xianbo Lu et al. (2005) developed a novel design for an amperometric gas sensor with the use of an yttria-stabilized zirconia (YSZ) porous layer which acts as an oxygen conductor and a gas diffusion barrier. The planar stack configuration was developed and allowed a deposition of YSZ layers. The device developed showed a linear output in the range of oxygen partial pressures. Ho and Hung (2001) also developed an amperometric NO_2 gas sensor based on Pt/Nafion electrode; NO_2 concentrations in the range of 0–485 ppm were detected. Similarly an amperometric hydrogen sensor was developed based on polymer electrolyte membrane with Nafion membrane as the conducting polymer. The response to hydrogen concentration was in the range of 260–11,500 ppm. Chao et al. (2005) developed an amperometric sensor using three different sensor designs for hydrogen and carbon monoxide sensing. The three different designs were tested under hydrogen and CO concentration, and devices II and III were found to have slower response times as compared to device I. Selectivity of the sensor under hydrogen concentrations was greatly improved by replacing Pt-air RE with modified Ag/AgCl RE and incorporating a semipermeable membrane. Amperometric gas sensors for the detection of hydrocarbon were reported by Dutta et al. (2005) for monitoring in exhaust pipes.

With the advent of microelectronics system (MEMS), microelectrodes with very small electrode surface area have been employed in the fabrication of electrochemical sensors due to their numerous advantages of having small size and weight, low cost, and faster response time without affecting the signal-to-noise ratio. Microamperometric sensors dated back in the 1980s consisted only of microfabricated electrodes on a suitable substrate; the earliest microamperometric sensor was developed by Sleszynski and Osteryoung in 1984 (La et al. 2011). Recently, techniques on how to improve the sensitivity of the sensors were reported by (Phawachalotorn et al. 2012).

10.2.7 Potentiometric Gas Sensors

Potentiometric gas sensors are used to determine the analytical concentration of some components of the analyte gas. They can measure the electric potential of an electrode without current flow. The signal is measured as the potential difference between the working electrode and the reference electrode. Potentiometric sensors have been used for oxygen detection. A typical potentiometric oxygen sensor is made up of an oxygen ion conducting solid electrolyte and two electrodes which are deposited on the two sides of the electrolyte. One of these is a reference electrode which is in contact with a known oxygen partial pressure, while the other is a working electrode which is in contact with an unknown oxygen partial pressure that needs to be measured. When the electrodes are in contact with two different oxygen partial pressures and isolated from each other, an EMF is developed by the sensor.

The electrodes are usually made from palladium, platinum, gold, or silver. Different electrolytes have been also used or a combination of two materials for the detection of different gases. Lee et al. (2001) developed a potentiometric CO_2 gas sensor using lithium phosphorus oxynitride electrolyte, while recently Jiun-Chan Yang et al. (Yang and Dutta 2010) developed a high-temperature NO_2 sensor fabricated with asymmetric reference and sensing electrode made with Pt and YSZ electrolyte. The combinations of these two materials have simplified the design and make it more compact. Similarly, Yan et al. (1995) developed a potentiometric sensor using stabilized zirconia for chlorine gas by combining MgO-stabilized zirconia tube with an auxiliary phase containing metal chloride with a sensitivity of 1–100 ppm of chlorine at 550–600 °C. With the advent of microfabrication technology, miniaturized sensors are produced so as to amplify the output of the potentiometric sensors. Radhakrishnan et al. (2005) fabricated a miniaturized series connected potentiometric sensor on a silicon fabricated electrode after using microfabrication techniques for oxygen detection.

10.2.8 Optical Gas Sensors

This type of sensors uses optical absorption/emission scattering of a gas species at defined optical wavelengths. An optical gas sensor consists of a light-emitting element, a photodetecting element, a gas-sensing element (the gas-sensing element responding to light), and a filter for picking up fluorescence or phosphorescence. Most optical sensors are usually based on thin films of palladium or chemochromic oxides coated along the length of an optical fiber. These types of fiber optic sensors are known as optodes. One of the most common optical gas sensors is infrared gas sensors which will be discussed later in more detail.

As shown by many authors, optical sensors have been used for many years in the detection of flammable gases like hydrogen. The first optical hydrogen gas sensor was reported by Butler (Hübert et al. 2011) in 1984 which consists of an optical fiber with palladium and titanium coatings. Detection of hydrogen was made using interferometry. Massie et al. (2006) also designed a low-cost portable optical sensor for methane detection with very good sensitivity; the sensor can operate even in harsh environments. Acquaroli et al. (2010) designed an optical porous silicon gas sensor. The system was tested over a detection area of the porous silicon microcavity with isopropyl alcohol vapor, and even small changes in concentrations were detected. Manap et al. (2009) developed an optical fiber sensor for the monitoring of ammonia gas using an open optical path techniques. Cross sensitivity of CO_2 and O_2 was also tested to see their effect on ammonia gas. Okazaki et al. (2003) also developed a fiber optic hydrogen gas sensor using catalyst-supported tungsten trioxide (WO_3). The sensor used platinic acid at 500 °C and showed good response toward hydrogen gas detection and can detect gas even at room temperature. Girschikofsky et al. (2012) recently reported an optical planar Bragg grating sensor which is capable of detecting substances like benzene, toluene, and xylene. Results obtained showed good sensitivity toward these gases.

10.2.9 Infrared Gas Sensor

Infrared sensors consist of a detector which converts electromagnetic radiation energy into electrical signals. The detectors are of different types, namely, thermoelectric, thermistor bolometer, pyroelectric detector, and photon detector. It also consists of an infrared source which could be a regular incandescent light or a heated wire filament which can be used for the detection of CO_2, CO, and other hydrocarbons. Another component is an optical fiber which could be of two types: dispersive and nondispersive.

Nondispersive types use discrete optical band-pass filters and are mostly used for gas sensor applications, while the dispersive types use an optical device like a grating or prism. The last but not the least is the gas cell which allows the light path so as to interact with the target gas. Infrared gas sensors are used for detecting different gases like methane, ethane, propane, butane, benzene toluene, and xylene and other alcohols like methanol, ethanol, etc. Okajima et al. (2006) developed an infrared gas sensor using LED for the measurement of methane; absorption of gas samples between 0% and 97% was successfully measured. Garcia-R et al. (2012) developed a nondispersive infrared (NDIR) gas sensor for the measurement of CO_2 gas concentration for wireless sensor networks with low power consumption. Similarly Chen et al. (2006a, b) designed a tunable diode laser absorption spectroscopy to produce a sensor that is miniaturized, and Zhang et al. (2010) developed a miniaturized CO_2 sensor based on infrared absorption.

There are two types of optical structure which is used for the construction of infrared CO_2 gas sensors, namely, time double beam and space double beams. The time double beam optical structure has only one infrared beam emitted from the infrared source, and the detector receives two infrared beams with different wavelengths and at different times, while the space double beam structure has one infrared beam emitted from the infrared source and simultaneously enters two parallel plate detectors. In this design, the space double beam is used so as to enhance the construction, and a cone-shaped air chamber is designed. The optical probe consists of an infrared source, an air chamber, an infrared receiving device, and two sapphire windows. The sensor showed an accuracy of 0.026% with CO_2 gas concentration in the range of 0–3%. Kasai et al. (2011) investigated the ability of a system using a carbon infrared emitter and an infrared camera to detect combustible gas propane.

10.2.10 Acoustic Wave Gas Sensors

Acoustic wave sensors are so named because their detection mechanism is a mechanical or acoustic wave. As the acoustic wave propagates through or on the surface of the material, any changes to the characteristics of the propagation path affect the velocity and/or amplitude of the wave. Changes in velocity can be monitored by measuring the frequency or phase characteristics of the sensor and can then be correlated to the corresponding physical quantity being measured. An acoustic wave sensor contains a receptor which is an element that is sensitive to an analyte and a transducer, i.e., an element that converts the response into an electrical signal.

The first acoustic gas sensor was discovered by King in 1964 (King 1964) and was based on the measurement of bulk acoustic waves (BAW) in a piezoelectric quartz crystal resonator which is sensitive to mass changes. After intensive research studies in mid-1960, chemical sensors for industrial atmospheric pollutants were developed. Since piezoelectric quartz resonators were used, these types of sensors were called quartz microbalances (QMB).

There are different types of acoustic wave sensors which are based on the type of wave propagation. Acoustic wave sensors have a variety of applications as in temperature, pressure, mass, chemical, etc. In this paper the application will be for gas sensing. The principle of operation of acoustic chemical sensor is described as follows. When a receptor film is introduced unto the vibrating surface of a transducer that is activated by an electronic device, the characteristics of the receptor film such as its mass and thickness are changed when exposed to an analyte. This change directly affects the vibration frequency, amplitude, and phase. The shift is directly proportional to the analyte concentration.

As reviewed by several works on different gas sensors, the current trend has taken the direction of developing the gas sensors using microelectronics technology due to its advantage of miniaturization and low power consumption. However, acoustic wave sensors already possess this inherent characteristic and were used in gas sensors since 1964, so this makes it to be an attractive candidate over its gas-sensing counterparts. A review on acoustic waves will be made in this section of the paper with emphasis on surface acoustic wave sensors. Another advantage of surface acoustic wave technology is that the gas sensing can be made wirelessly as shown by (Lim et al. 2011), which makes real online monitoring of the gas sensor possible and eliminates the use of wired cables. This property makes it an attractive candidate for gas detection and makes it superior to other gas-sensing techniques. Also high selectivity and sensitivity have also been reported in many SAW gas-sensing applications (Dutta et al. 2005; Yang and Dutta 2010; Radhakrishnan et al. 2005).

Surface Acoustic Wave Gas Sensors

Surface acoustic wave technology refers to the use of the SAW device in several technological applications. Surface acoustic waves were first discovered by Lord Rayleigh in 1885. SAW sensors are developed based on Rayleigh waves. A Rayleigh SAW is made up of two mechanical displacement components in the sagittal plane, i.e., the plane containing the direction of propagation and the surface normal. For gas-sensing applications, the choice of piezoelectric substrate determines the type of SAW wave. Rayleigh waves propagate in a thin surface layer and can penetrate into the substrate at a distance of the order of a wavelength. The velocity of propagation of the wave depends on the substrate material, the crystal cut of the substrate, and the working frequency (Hübert et al. 2011).

Since after the discovery, a lot of potential applications have been exploited which among them are the sensor applications including chemical, optical, thermal, pressure, acceleration, torque, and biological. The main advantages of using SAW technology are high sensitivity, low power consumption, being wireless, and can be placed on moving or rotating parts and in hazardous environment. The SAW device is also technologically compatible because its fabrication process is similar to that of other microelectronic devices.

Principle of Operation

Surface acoustic wave sensors work based on the principle of transduction whereby the sensor converts an input electrical signal into a mechanical wave and reconverts back into electrical signal. This is made possible by means of the interdigitated transducer known as the IDT which uses the piezoelectric effect. The IDTs are made of electrodes made from aluminum, gold, or platinum. A typical SAW therefore consists of an input and output transducer with spacing between them called a delay line. The principle of gas sensing in SAW is realized by the application of a sensing

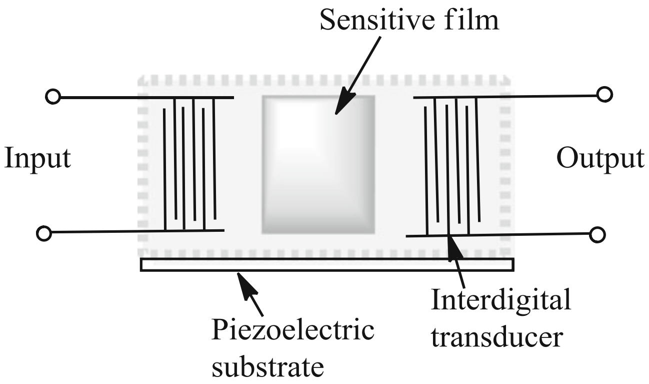


Fig. 10.4 A SAW device to depict the principle of gas sensing

material like a thin polymer across the delay line which selectively absorbs the gas or gases of interest as depicted in Fig. 10.4.

Rayleigh SAW sensors are based on two types of acoustoelectronic devices, namely, delay line and resonator. The frequency of operation of Rayleigh wave's sensors usually lies between 40 MHz and 600 MHz. These devices differ from each other in their design. A delay line has two receiving and transmitting interdigital transducers, whereas a resonator has one interdigital transducer placed at the resonator cavity. However, their mechanism of response is the same, and they also have similar output characteristics. A delay line is simpler to design compared with the resonator; that is why it is mainly used for practical applications. However, a delay line requires matching due to the insertion attenuation and is subjected to having oscillation frequency, but the resonators have smaller attenuations and do not require matching (Fischerauer et al. 1996). A resonator and a delay line could be either single- or two-port. A single-port delay line consists of a propagation path between one IDT and one or more interdigital reflectors. A two-port SAW delay line consists of a propagation path between two separate IDTs: the first serves as a transmitting transducer, and the second serves as a receiving transducer so as to convert the SAW back to electrical form.

10.2.11 SAW-Based Gas Sensors

Surface acoustic waves were the next generation of acoustic wave sensors after the advent of the quartz crystal microbalance (QCM) which was used to stabilize the frequencies of radio transmitters and later modified by the addition of sorptive film on the crystal so that it could be used for chemical sensing. Subsequently the device was analyzed and improved by some researchers in the 1950s. In the late 1970s, Wohltjen and Dessy (1979) realized that chemical vapor sensing could be accomplished with a device that was originally used for processing of electrical signals which is the SAW delay line.

Since then a lot of researchers have been working on SAW sensors for detection of different gases which are either toxic, harmful, or pollutants, while others can be used as fuel gases in industries and automobiles. Researchers tend to employ SAW resonator if their prime interest is to control the center frequency, whereas if the time response is of interest, they decide to use the delay line. SAW delay line is commonly used due to its simplicity in the design and fabrication. M. S. Nieuwenhuizen et al. (Nieuwenhuizen and Nederlof 1990) developed a SAW gas sensor for detection of CO_2 and H_2O using dual delay-line oscillators on a quartz substrate at a frequency of 40 MHz. Venema et al. (1987) also designed a SAW delay-line gas sensor using quartz substrate for the detection of NO_2 gas. Subsequently, Anisimkin et al. (1995) also developed a SAW delay-line gas sensor for the detection of CO, NO, hydrogen, and oxygen gases, respectively. Beck et al. (1999) also developed a SAW delay line using lithium niobate substrate for the detection of NO_2 and methane gases. A review paper was published recently by Wieslaw P. Jakubik on dual delay-line oscillator. However, Lee et al. (1997) designed SAW resonator gas sensor using lithium niobate for the detection of methane and hydrogen gas. Similarly, Fischerauer et al. (1996) also employed a SAW resonator for the detection of hydrocarbons. Due to the good results displayed by the use of SAW devices for gas sensing in terms of high sensitivity, selectivity, and good response times, a lot of researchers are working extensively so as to detect different gases using different configurations of SAWs and at different frequencies. Results obtained have produced excellent results in terms of high selectivity, high sensitivity, and good response times.

10.2.12 Semiconductor Gas Sensors

Semiconductor gas sensors are devices that are made up of heated metal oxides which are used for measurement of gas concentration of a target gas by measuring the electrical resistance of the device. They work on the principle of reversible gas adsorption process at the surface of the heated oxide, usually oxides of tin deposited on a silicon slide by chemical vapor deposition method. Absorption of the sample of gas on the oxide surface followed by catalytic oxidation results in a change of electrical resistance of the oxide material which is then related to the sample gas concentration which is monitored by the meter as shown in Fig. 10.5. The heater at the base is used for heating up the sensor to a constant temperature of about 200–250 °C so as to speed up the reaction rate (Hassan et al. 2013, 2014a, b, c).

An intrinsic n-type semiconductor is suitable for detecting reducing gases due to the high conductance change as a result of the injected electrons. Similarly, a p-type semiconductor is suitable for the detection of oxidizing gases. The oxides usually used for the n-type are mainly oxides: SnO_2, ZnO In_2O_3, or WO_3 (Hassan et al. 2014a, b, c). They are commonly used to detect hydrogen, oxygen, alcohol, and

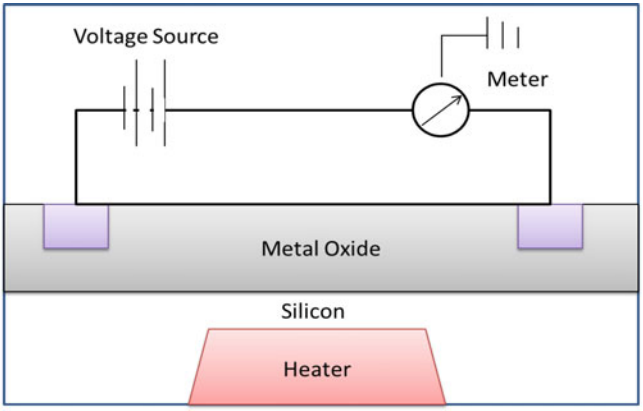


Fig. 10.5 A typical semiconductor sensor

harmful gases like carbon monoxide. Gas sensors using metal oxide semiconductor were first proposed by Seiyama and Taguchi. When inflammable gases come into contact with metal oxides, they excite a new electron level within the solid and thus cause a change in electrical resistance of the gas-sensing elements. Jin Huang and Qing Wan published a review paper on the progress in gas sensors based on semiconducting metal oxide one-dimensional (1D) nanostructures (Dey 2018).

It was reported that due to the advent of microelectronics, new device structures such as the electronic nose and the low power consumption self-heated gas sensor have been designed, and their response has been evaluated (Huang and Wan 2009). Sensitivity and selectivity could be improved by the addition of small amounts of noble metals like Pd-added elements. Khodadadi et al. (2001) reported on improving the sensitivities of methane and carbon monoxide gases by adding 5% of K_2O into SnO_2 samples; the sensitivity was improved by 40%.

Similarly, 5% of Na_2O in SnO_2 layers showed reduction of sensor sensitivity to CO. Addition of platinum into the prepared samples improves the response to methane. However, improved sensitivity could also be obtained by the addition of doping agent in thick-film semiconductor gas sensor developed for the sensing of methane and butane. The semiconductor gas sensors have different configurations, one-electrode and two-electrode configuration.

Operation Principle of One-Electrode Semiconductor Gas Sensors

The one-electrode sensor configuration is depicted in Fig. 10.6; as reported by Korotcenkov (2007a, b), the metal resistor acts as both the heater and measuring electrode at the same time. One-electrode sensors are similar to pellistors or hot-wire sensors. The operation principle of one-electrode sensor is based on the shunting of the Pt wire by semiconductor oxide coating the metal spiral. The one-electrode sensors are typically incorporated in a Wheatstone bridge circuit, and they work

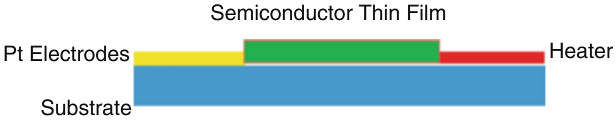


Fig. 10.6 Showing one-electrode configuration of semiconductor gas sensor

under a stabilized constant current. The shunting semiconductor resistance should be ensured to have a resistance value of the same order of magnitude as that of the Pt resistor at the operation temperature. Due to the low heater resistance, only metal oxides with high conductivity are capable of changing the total resistance of sensors in the presence of gases detected. For one-electrode semiconductor sensor design, SnO_2 and In_2O_3 have been used. However, the two-electrode configuration will not be discussed because it is not very common.

The gas-sensing materials for one-electrode sensors are deposited using chemical vapor deposition (CVD), physical vapor deposition, and sol-gel process. Recently, Shimanoe et al. (2011) developed a semiconductor nano-sized oxide for the detection of inflammable gases, odor gases, and other environmental-related gases using MEMS technology with low power consumption. Takada (2000) developed a new method for gas identification of different gases including hydrogen, carbon monoxide, methane, and volatile organic compounds. Recently, artificial intelligence techniques are integrated into gas sensors as shown by Byeongdeok Yea et al. (Konishi 1997).

In order to improve sensitivity of the sensor, different methods had been used including temperature modulation, synthesis of new sensor materials, designing new sensor constructions, adoption of new filter layers, and using of sensor array. Therefore, Halek et al. (2009) made a comparison of methods of selectivity improvements of semiconductor gas sensors and concluded that the kind of sensing material and filter layer has a strong influence on the sensor parameter.

Sensing Materials of Semiconductor Gas Sensor

From the first tin dioxide sensor developed in the 1970s for domestic gas alarms, there has been an increase in the demand for high-performance solid-state gas sensors. Results of a search study on metal oxide semiconductor (MOS) used as sensing materials for solid-state gas sensors, including both the n-type and p-type oxides, are summarized in the graph shown in Fig. 10.7 (Kim and Lee 2014).

Metal oxides stand out as one of the most common, diverse, and, most likely, largest class of materials due to their extensive structural, physical, and chemical properties and functionalities. The most common metal oxides utilized as sensing layer in gas sensor devices are binary oxides such as SnO_2, ZnO, TiO_2, etc.; however, ternary and more complex oxides are also applied in practical gas sensors (Huang and Wan 2009).

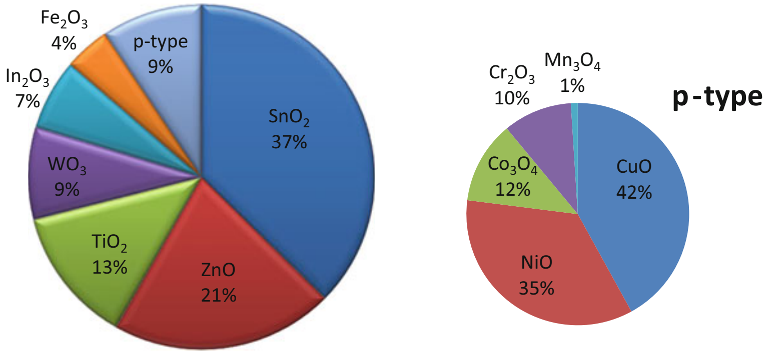


Fig. 10.7 Studies on n- and p-type oxide semiconductor gas sensors

SnO_2 is the most extensively studied metal oxide and is widely applied in practical commercial devices. Tin dioxide is a wide band gap (3.6 eV) semiconductor with interesting electrical properties (Ogawa et al. 1982). Due to its high sensitivities for different gas species, tin oxide-based sensors allow the detection of low concentration levels of gaseous species, though it unfortunately suffers from the lack of selectivity. Nevertheless, strategies devoted to enhance the SnO_2-based device's performance have been extensively studied (Korotcenkov 2005).

Zinc oxide is a II–VI semiconductor showing a wide band gap (3.37 eV), with the dominant defects identified as O vacancies (Mahmood et al. 2013). ZnO has attracted much attention in the gas-sensing field because of its high mechanical and chemical stability, suitability to doping, nontoxicity, and low cost. The sensing property of ZnO is strongly influenced by the nanostructural features, such as the grain size, geometry, and connectivity between the grains (Kashyout et al. 2010).

Titania is particularly attractive for gas sensors because of its lower cross sensitivity to humidity than other metal oxides (Tricoli et al. 2009). Among the other applications, TiO_2 has been largely investigated as a sensing layer in resistive oxygen gas sensors operating at medium to high temperatures for automotive air/fuel ratio control. At medium temperatures (400–600 °C), oxygen detection is mainly due to reactions that takes place on the surface, whereas at high temperatures (700–1000 °C), oxygen detection is mainly due to diffusion of oxygen ions in the bulk of the material (Ramamoorthy et al. 2003).

A lot of factors affect the gas sensor performance of metal oxide which, in turn, is determined by the reception and transduction function along with the fabrication procedure (Yamazoe and Shimanoe 2009). The synthesis procedure, crystal size and shape, and the addition of foreign elements with the role of sensitizers or conductivity modifiers are some of the factors influencing the sensor response (Aleixandre and Gerboles 2012; Huang and Choi 2007; Jimenez-Cadena et al. 2007).

Doping the metal oxide layer with suitable promoters (metal particles, other metal oxide, and ions) is a common way of enhancing the sensing characteristics of gas sensitivity. The modification of the sensing properties of the sensing material by the introduced additives depends on the nature of the latter (Hassan et al. 2014a, b, c).

For example, Pt is known to promote the gas-sensing reaction by the spillover of sample gas (chemical sensitization), whereas Pd is known to promote the gas-sensing reaction by electronic interaction between Pd and sensing materials (electronic sensitization) (Cabot et al. 2000).

The grain-size reduction at nanometric level is one of the main factors enhancing the detection properties of metal oxides. It is in fact well recognized that by reducing the particle size of the sensing material in the nanometer range, the sensitivity of gas sensors is greatly improved both for the large specific surface offered and for the influence in reducing the surface charge density (Dolbec et al. 2003; Korotcenkov 2008; Rothschild and Komem 2004a, b). Furthermore, in this size range, a large fraction of the atoms (up to 50%) are present at the surface or the interface region. Therefore, the chemical and electronic of nanoparticles are different from those of the bulk, consequently contributing to an increase in the sensing properties.

Over the last 50 years, novel sensing materials other than metal oxides have been proposed. In 1983, the gas-sensing properties of conducting polymers were first reported. The sensor involved the use of doped polypyrrole (PPy), functioning as an ammonia sensor. In fact, as the conductivity of the pure conducting polymer is rather low, in order to achieve the high conductivity suitable for sensing applications, a doping process was necessary (Fig. 10.8). A wide variety of polymers of this type is now available, including substituted polypyrroles, polythiophenes, polyindoles, and polyanilines (Hassan et al. 2015).

Organic materials are much more easily modified than inorganic materials with respect to such characteristics as sensitivity, working temperature, and selectivity. Long-term instability is a main drawback of the sensors based on conducting polymers as they are thermally unstable, so it is often impossible to use them at temperatures at which gas-solid interactions proceed rapidly and reversibly.

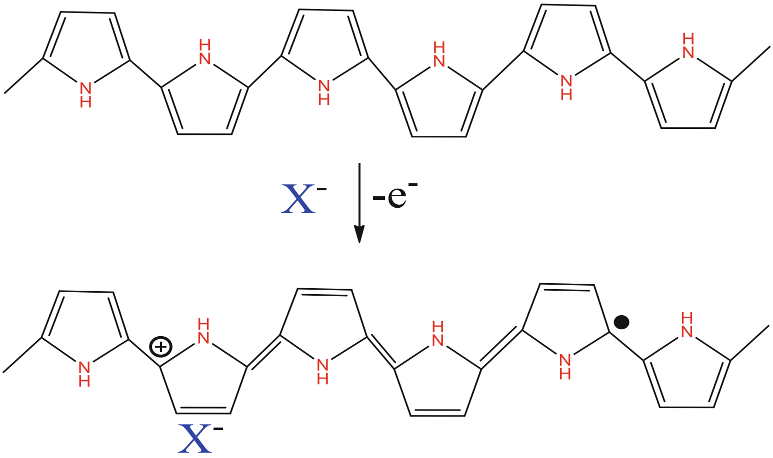


Fig. 10.8 Molecular structure of polypyrrole (PPy) and related doping process

To fully use all the potential advantages of organic and inorganic materials, hybrid composites have also been introduced as sensing elements for resistive sensors (Jiang et al. 2013). These hybrid organic/metal oxide composites are not merely the sum of the individual components but rather new materials with new functionalities and properties. From the viewpoint of structure, organic support can induce the nucleation, growth, and formation of fine metal oxide nano-/microstructures with uniform dispersion and controlled morphology, thereby avoiding the agglomeration of metal oxides. If the organic component is a good electrical conductor (e.g., conductive carbon, carbon nanotubes, or graphene), the resulting composites can form a perfect integrated structure with a developed electron conductive network and shortened current transport paths, improving the poor electrical properties and charge transfer of pure metal oxides. Significant synergistic effects, such as room-temperature sensing capability when exposed to low-concentration gases such as NO_2, H_2, and CO, often occur in hybrid composites because of size effects and interfacial interactions in contrast to the high-temperature operation required for metal oxides alone.

The possibility of synthesized materials having dimensions in the order of nanometers has provided enormous advantages for gas sensing because their extremely high surface-to-volume ratio is ideal for gas molecule adsorption. One important example is that of carbon nanotubes (CNTs), which are currently receiving a great deal of interest in gas sensing. Dai et al. first demonstrated the variety that they can offer for practical applications in highly sensitive gas sensors (Kong et al. 2000). The high surface-to-volume ratio, high conductivity, and mechanical stability make CNTs very attractive for gas-sensing applications. Carbon nanotubes can now be synthesized by different methods in large quantities and with high purity, such as the chemical vapor deposition (CVD) technique, and can be doped with B and/or N groups, thus rendering them very sensitive to a wide range of gas vapors (Peng and Cho 2003). In a similar way, functionalizing the nanotube surface with the polar COOH group attached, the sensors will give stronger responses toward the volatile organic compounds (VOCs) as their absorption efficiency with these volatile organic molecules will be increased due to the dipole-dipole interactions (mainly hydrogen bonding) between the COOH and the polar organic molecules (Sin et al. 2007).

CNTs are also often used as carriers of supported metal oxide particles (Sun et al. 2002). CNTs provide high surface area and then help the dispersion of the sensing materials on the nanotube walls. The better performance of these hybrid sensors is also attributed to the effective electron transfer between the metal oxide particles and the highly conductive carbon nanotube network (Lu et al. 2009a, b; Sun et al. 2012; Willinger et al. 2008). CNTs could also be coated with metal oxides of controlled thickness (Marichy and Pinna 2013). By combining the nonaqueous sol-gel route with the atomic layer deposition, metal oxides have been grown from the respective metal alkoxide precursors at low temperatures. Moreover, the surface reaction leading to the M-O-M bond formation is self-limited and allows then the deposition of films with well-controlled thickness on the internal and external surface of CNTs.

The successful synthesis of nanoparticles, nanowires, nanotubes, and other shapes has generated a lot of work to use these nanostructured materials in gas sensing (Lu et al. 2006; Pan et al. 2001; Li et al. 2003; Comini 2006). In particular, low-dimensional structures of metal oxides were found to possess characteristics and enhanced gas-sensing properties. In 2002, the Sberveglieri and Yang groups initiated the investigation of gas-sensing properties of one-dimensional nanostructures (Comini et al. 2002; Law et al. 2002).

Hierarchical and hollow oxide nanostructures are also very promising gas sensor materials due to well-aligned nanoporous structures with less agglomerated configurations. The literature data clearly show that these peculiar nanostructures can increase both the gas response and response speed simultaneously and substantially (Lee 2009). This can be explained by the rapid and effective gas diffusion toward the entire sensing surfaces via the highly porous structures.

Working Mechanism of Metal Oxide Semiconducting

Along with the improvement of the characteristics and properties of the devices, a great deal of effort has been also made during these years to improve knowledge of the sensing mechanism and understanding the related processes. The description of mechanisms of gas sensors based on metal oxides was first depicted through the application of electron theory of chemisorption and catalysis on semiconductors originally formulated by Wolkenstein (1961).

Later, Morrison, Yamazoe, and Gopel especially contributed to the description of conditions of transport of electric charges through the metal oxide semiconducting layer in the presence of oxygen and reactive gases (Morrison 1982; Yamazoe et al. 1983; Gopel and Schierbaum 1995). Following these theories, the sensing mechanism of MOS sensors relies on reactions which occur between adsorbed oxygen species and the probed gas on the surface of the sensing layer. Details on this subject can be found in many books and reviews (Azad et al. 1992; Barsan et al. 1999). In first approximation, oxygen adsorbed on the surface of n-type metal oxide semiconductors plays a key role, trapping free electrons because of its high electron affinity and forming a potential barrier at the grain boundaries. This potential barrier restricts the flow of electrons, causing the electric resistance to increase. When the sensor is exposed to an atmosphere containing reducing gases, e.g., CO, the gas molecules adsorb on the surface and react with active oxygen species, e.g., O^-, which liberates free electrons in the bulk. This lowers the potential barrier allowing electrons to flow more easily, thereby reducing the electrical resistance. With oxidizing gases such as NO_2 and ozone, the adsorption process increases instead the surface resistance (Leblanc et al. 2000). The converse is true for p-type oxides, where electron exchange due to the gas interaction leads either to a reduction (reducing gas) or an increase (oxidizing gas) in electron holes in the valence band (Li et al. 2002). However, to give a complete description of the gas-sensing mechanism for these sensors, it is necessary to take into account all elementary steps (adsorption, reaction, desorption, etc.) governing surface-gas target interactions leading to charge transfer (Yamazoe and Shimanoe 2008).

Yamazoe first demonstrated that reduction in crystal size would significantly increase the sensor performance (Yamazoe 1991). The sensing properties are partially associated with the depth of the surface space charge region which is affected by the gas adsorption and depends on the particle size. Specifically, the sensor's response increases significantly if the crystallite size is about twice the adsorption depth, 2L (L is the depth of the space charge layer), of oxygen adsorbates. This means that the sensor performance improves not only when D decreases but also if L increases, since a major proportion of material takes place in the reaction of oxygen adsorbates with the target gas even if the grain size is not excessively small. For a typical sensing material, SnO_2 with different grain sizes between 5 nm and 80 nm, simulations showed that the conductivity increases linearly with decreasing trapped charge densities and the sensitivity to the gas-induced variations in the trapped charge density increases too, in agreement with experimental findings (Rothschild and Komem 2004a, b).

When dealing with wire with lateral dimensions to the order of hundreds of nanometers, gas adsorption creates a surface depletion layer, consequently reducing the conducting channel thickness (Chen et al. 2013). The mobility dependence on surface coverage can be neglected because electron diffusion length (about 1 nm) is much shorter than the diameter (tens of nanometers). Electrical transport changes when the thickness of the wire is small like in nanowires with low lateral dimensions compared to the Debye length, the space charge region extends through the entire wire cross section, and all electrons are trapped in surface states (Zhu and Zeng 2017).

A model of the sensing mechanism of hybrid heterostructures such as metal oxide/CNTs has been attempted. The junctions existing between the nanotubes of the networking at their crossing points and the different depletion regions existing as a function of the presence of the target gas have been taken into account. Their role in the sensing mechanism has been established by several authors (Wei et al. 2004; Marichy et al. 2013).

Sensing Materials: Effect of Grain Size and Film Thickness

The most traditionally used materials for solid-state gas sensors are thick films of polycrystalline compressed or sintered MOS powders. In the case of compressed powders, the grain-boundary resistance dominates the response of the sensor device since the resistance at these intergranular contacts is much larger than the resistance across a single grain. Compressed powders are not very stable as the intergranular contact is pressure sensitive. In sintered powders, some of these grain boundaries disappear and form more stable neck-like structures as the grains sinter together. These necks often constitute the most sensitive sites of sensing materials as all the electrons from these narrow necks are potentially tied up with the adsorbed oxygen, giving rise to very sensitive completely electron-depleted highly resistive regions.

In Fig. 10.9, we illustrate the energy band model for an MOS compressed powder. A few grains are shown where chemisorbed oxygen has captured electrons

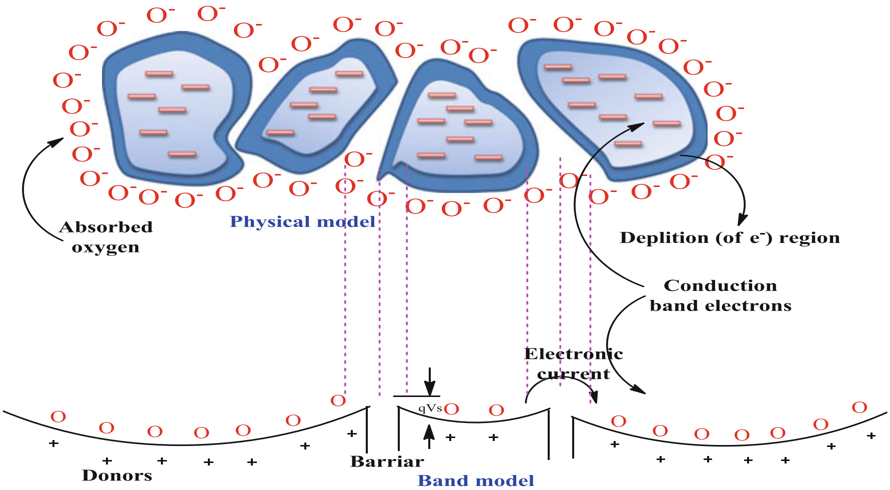


Fig. 10.9 Three grains of a semiconductor oxide showing how the intergranular contact resistance comes about

from the material forming a depletion layer (also known as the space charge layer or the Debye layer). At the intergranular contact, two space charge layers back to back form a formidable barrier for electrons to cross, and this gives rise to the higher resistance values at those contact points. The thickness of the depletion layer or the Debye layer (L) is relatively small compared with the grain diameter (D) in most traditionally polycrystalline materials. A typical value for L is 100 nm for MOS films. Grain-boundary-controlled gas sensing, most important for relatively large-particle MOS sensors, has been extensively reviewed by Barsan and Weimar (2001, 2003). In this contribution, we use these early sensing models to gain an understanding about what to expect when particle size decreases to the nanometer range.

When an MOS gas sensor is exposed to reducing gases, such as H_2, CO, and CH_4, at a sufficiently high temperature, the chemisorbed oxygen reacts with the reducing gases, lowering the steady-state surface coverage of the oxygen while injecting electrons into the MOS crystallites and thus lowering the height of the potential barriers at the intergranular contacts (qV_s in Fig. 10.1). The important reactions involved in this type of gas sensor may thus be summarized as follows.

Oxygen Reactions

$$\mathrm{MO} + \mathrm{O} + e^- \rightarrow \mathrm{MO} - \mathrm{O}^- \left(\text{between } 150^\circ\mathrm{C} \text{ and } 300^\circ\mathrm{C}\right) \tag{10.6}$$

$$\mathrm{MO} + 2\mathrm{O} + e^- \rightarrow \mathrm{MO} - \mathrm{O}_2{}^- \left(\text{between } 30^\circ\mathrm{C} \text{ and } 150^\circ\mathrm{C}\right) \tag{10.7}$$

As a result, electrons are extracted and resistance goes up.

Reducing Gas Reactions Reducing gas molecules (R) react with the chemisorbed oxygen at the grain boundaries and/or necks:

$$R + MO - O^- \rightarrow MO + RO + e^- \qquad (10.8)$$

As a result, electrons are injected and resistance goes down.

Also, oxidizing gases can be detected. The oxidizing reactions may be summarized as:

$$MO - O^- + O + e^- \rightarrow MO - O_2{}^- \qquad (10.9)$$

As a result, electrons are extracted and resistance goes up even further. Therefore, by measuring the change in the conductivity of the semiconductor oxide films, one can detect reducing and oxidizing gases in the atmosphere.

The above analysis of the MOS sensing mechanism, for the sake of clarity and brevity, is somewhat simplified. Indeed, not only a change in the number of free electrons (and thus boundary layer thickness modulation) but also changes in electron mobility may modulate the sensing response, as investigated by Ogawa et al. and recently reviewed by Tricoli et al. (Ogawa et al. 1982; Tricoli et al. 2010). Furthermore, there is still an ongoing debate in the MOS gas sensor community about the possibility of another sensing mechanism altogether. Gurlo and Riedel (2007) point out that, although it has been sought for a long time, there is not yet any convincing spectroscopic evidence for oxygen “ionosorption” as shown in Fig. 10.1. In their alternative model, there is no oxygen ionosorption on the MOS surface, and the model focuses instead on oxygen vacancies at the surface, which are considered to be “the determining factor in the chemiresistive behavior” (Zemel 1988). SnO_2, the model gas-sensing material, is oxygen deficient and therefore acts as an n-type semiconductor, with oxygen vacancies that act as electron donors. Alternate reduction and reoxidation of the surface by gaseous oxygen control the surface conductivity and therefore the overall sensing behavior in this model.

Catalysts such as Pt enhance gas-sensing reactions of MOS via the spillover effect. Spillover refers to the process in which the catalyst dissociates a gas molecule, and then the atoms “spill over” onto the surface of the MOS. At the right temperature, a gas reactant first adsorbs onto the surface of the catalyst particles and then migrates to the oxide surface to react there with reactive surface oxygen species. For this process to be possible, the spilled-over species must be able to migrate to the interparticle contact (grain boundary or neck). As a consequence, for a catalyst to be effective, there must be a very good dispersion of the catalyst particles so that they are available near all contacts. Only then can the catalysts affect the interparticle contact resistance that controls the gas sensor sensitivity. Importantly, in the case of nanoparticles, there are several reports which indicate that the need for metal catalysts is somewhat alleviated (Rothschild and Komem 2004a, b; Cukrov et al. 2001).

Porosity, grain size, and film thickness all play an important role in the LOD and sensitivity of MOS gas sensors. Lee et al. (2000) carried out a comparative study of thick- and thin-film SnO_2 gas sensors in order to understand the differences in gas-sensing characteristics as a function of the microstructure of the gas-sensing

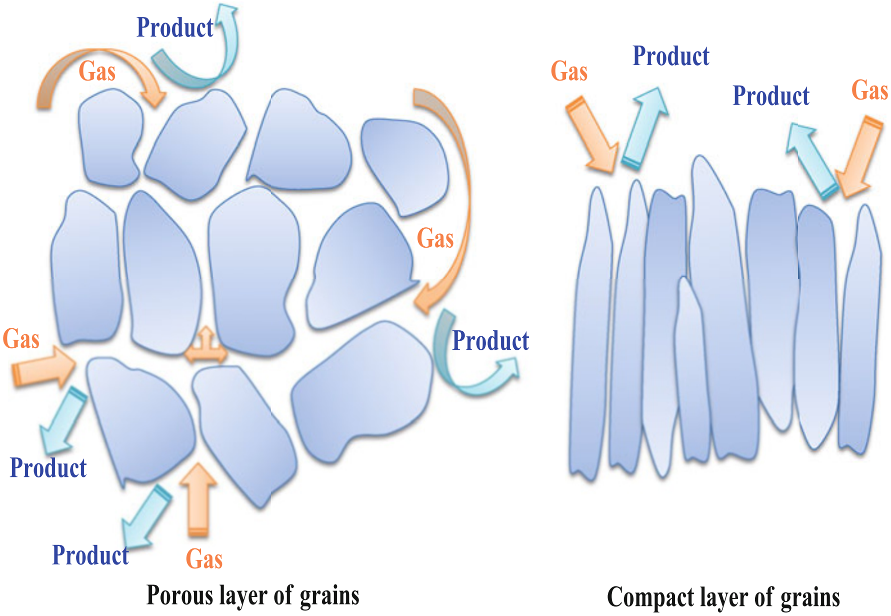


Fig. 10.10 Schematic of a gas-sensing reaction in (**a**) the compact layer and (**b**) the porous layer

materials. Thin films, in their investigation, were deposited using metal organic chemical vapor deposition (CVD), which yielded a dense compact microstructure (Fig. 10.10). Thick porous films were derived from metal organic decomposition. These thick films were made up of a network of loosely connected crystallites that also featured several cracks (approx. 1 mm wide) as well as small pore channels at the crystallite surfaces that all help in the penetration of gas molecules throughout the material and thereby enhance the sensitivity (Fig. 10.10). Lee et al. confirmed a much improved gas sensitivity in the case of porous thick-film microstructures compared with compact thin layers of SnO_2. In a porous MOS film, grain boundaries are present in all directions, and more surface area is available for reactions (R1)–(R3) to take place. In a compact film, on the other hand, only a limited exposed surface area is affected by the presence of analyte gases. Therefore, porous films are superior for gas-sensing purposes. In Fig. 10.2, we illustrate the surfaces that are likely to participate in the resistance change of these two types of MOS gas-sensitive material configurations.

Since the sensitivity of the high-surface-area porous gas sensors resides in the high resistivity grain-boundary contact points, one wants to make the number of these contact points as high as possible. So a thicker porous film is better. One also wants to make these contact points as stable as possible. A powder that is not sintered is pressure sensitive and quite unstable. In order to improve this, the MOS powders are sintered, giving rise to the formation of necks between the grains in the powder. The sensitivity of the film depends very much on the extent of the sintering of the

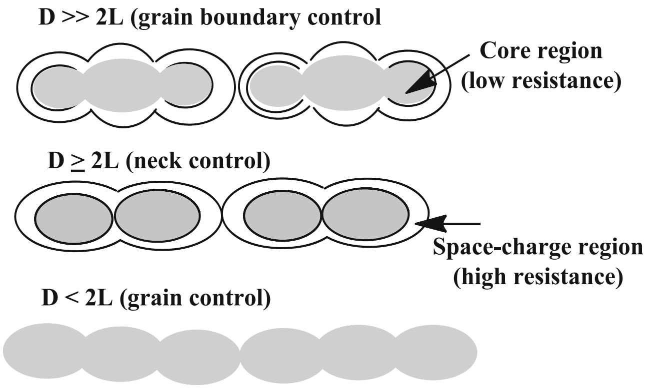


Fig. 10.11 Schematic models for grain-size effects

material. One should not sinter so much that the film becomes one compact layer, reducing the porosity and thus the sensitivity of the sensor dramatically. In most sintered MOS films, both necks and grain contacts are present. Neck-grain models with different degrees of neck formation have been investigated by several research groups.

Xu et al. (1991) proposed a model with a chain of crystallites connected mostly by necks and sometimes by grain-boundary contacts. These authors assumed the neck size (X) 0.8 times the crystallite size (D) and suggested that, when D is larger than 2L, grain-boundary contacts display higher resistance and govern the electric gas sensitivity of the chain (grain-boundary control). As D becomes smaller and comparable to 2L, necks become most resistant, and therefore they start controlling the gas sensitivity (neck control). Finally, when D is smaller than 2L, the resistance of grains dominates the whole resistance of the chain, and the gas sensitivity in this case is controlled by grains themselves (grain control) and yields the largest gas sensor response.

Figure 10.11 demonstrates the three situations. Along the same line, Rothschild and Komem [19] showed that the gas-induced variations in the trapped charge density in the MOS are proportional to 1/D, where D is the average grain size. At the nanoscale, the grain size can be decreased to match the Debye layer (L) thickness (typical value is 100 nm – see above), or can even be made smaller, which leads to the extraction of all electrons by the chemisorbed oxygen present. Such nanostructures can thus be treated as gas sensor materials with uniformly changing resistance upon exposure to gases (see grain control in Fig. 10.11).

Ma et al. (2002) carried out a theoretical study to better understand the dependence of the grain-boundary potential barrier as a function of the density of electrons trapped at the surface (n_t) and electron density in the bulk of the material (n_b). These authors suggest a model for neck-grain boundary control in order to investigate the combined effect of neck and grain boundaries in a sintered powder. For a constant distribution of such donors, the height of the grain-boundary potential barrier (eV_s; see Fig. 10.9) is

$$eV_s = \frac{e^2 n_t^2}{2\,\Sigma_0\,\Sigma_r\,n_b} \tag{10.10}$$

where e is the electron charge, n is the surface electron density, $\Sigma_o \Sigma_r$ is the permittivity, and nb denotes the free electron density in the grain body.

Assuming that the necks in a sintered ZnO powder are cylindrical, resistance values were calculated for both neck and grain boundaries employing Eq. 10.10. Like Xu et al. (1991), these authors concluded that gas sensitivity increases with decreasing grain size, which results from increased neck control. From this discussion, we can also appreciate that, in the case of a thin compact film, one likes the thickness to be small, perhaps in the range of L or less, so as to have a completely electron-depleted thin film.

We can conclude from the discussions so far on grain size, porosity, and thickness that, for the best gas sensor performance, we need a thick film of lightly sintered nanocrystalline, porous material. Nanocrystalline metal oxides offer other advantages as well; they can operate at lower temperatures and might obviate the need for expensive catalysts (Wang et al. 2010). Some words of caution are in order here with respect to the ultimate MOS grain size and the optimal film thickness.

Nanomaterials do indeed not come without disadvantages. Especially, thermal instabilities are worrisome since smaller MOS grains tend to agglomerate at lower temperatures, and this leads to changing sensor characteristics over time. Thermal degradation is responsible for temporal instabilities in device parameters and higher drift rates. According to Korotcenkov and Cho (2010), the larger the grain size, the wider the temperature range in which crystallites retain their size and shape without changes. Conversely, the smaller the grain size, the lower the temperature at which structural changes start taking effect; for example, films with a grain size of 2–3 nm start transforming at temperatures of approximately 200 °C. The same authors concluded that very small (approx. 20 nm) particles of SnO_2 and In_2O_3 MOS materials are not quite suitable for gas sensing above 500 °C, as the particles melt and agglomerate at much lower temperatures than their respective bulk melting points. An optimum approach that balances a high sensitivity by decreasing the particle size with good stability, calibration frequency, and lifetime requirements of a commercial gas sensor is therefore recommended. Above, we advocated making porous, lightly sintered nanoparticles into a thick film for the ideal gas sensor characteristics. On the other hand, some reports have shown that reducing the film thickness does increase the sensor's response considerably (Tricoli and Pratsinis 2010). This is in agreement with models of MOS sensor response to several analytes (Becker et al. 2001) and has been discussed in detail recently by Tricoli et al. (2010). Without more detailed studies, this is a hard argument to settle; indeed particle size, degree of sintering, and thus porosity are all intertwined. Depending on the porosity and particle size, either a thinner or a thicker film might be required.

MOS nanocatalysis can be considered as a bridge between homogeneous and heterogeneous catalysis. Because of their nanosize, i.e., high surface area, the contact between reactants, gas sensors, and nanoparticles is huge. Pinna et al. (2004), for example, demonstrated that gas sensors based on tin and indium oxide nanopowders exhibited high sensitivity and good recovery time at low temperature. Especially, indium oxide nanoparticles were highly sensitive toward NO_2 with a detection limit of 1 ppb at low temperatures.

Nanobelts (nanowire-like structures but with flat cross sections), nanorods, and nanowires have all been successfully implemented as gas sensor materials and continue to be investigated for their potential advantages over traditional materials. These nanomaterial-based gas sensor devices are based either on mass assemblies of nanoparticles (e.g., porous mats) or on one or a set of individual nanoparticles (e.g., a small number of nanowires) (Sadek et al. 2007; Lee et al. 2008; Wang et al. 2008).

Sadek et al. (2007), for example, developed a conductometric H_2, NO_2, and hydrocarbon gas sensor using a ZnO nanobelt film as the sensitive layer. In Sadek et al.'s experiments, ZnO nanobelts display a structural morphology (wurtzite family) characterized by a rectangular cross section and a uniform long structure along their length. A mat of these nanobelts was deposited by radio frequency (RF) sputtering on a heater element.

The sensing elements in sensors fabricated by Lee et al. (2008) are thin films consisting of SnO_2 nanorods. The nanorod films also were equipped with well-dispersed Pd catalyst nanoparticles with an average diameter of 3 nm. These thin-film nanorods were deposited using plasma-enhanced CVD (PECVD) with post-plasma treatment. The surface of these nanorod thin films was modified with Pd nanoparticles, and the sensing properties of the thus fabricated films were tested with H_2 and ethanol vapors. Yeom et al. (2008) employed nanomembranes for pre-concentration of gases that were detected using a microfluidic sensor that resulted in much enhanced sensitivity.

In another study by Liu et al. (2006), vanadium oxide nanobelts coated with MOS nanoparticles such as Fe_2O_3, TiO_2, and SnO_2 were employed as hybrid sensor nanostructures for sensing ethanol vapors. These vanadium pentoxide (V_2O_5) nanobelts coated with MOS nanoparticles showed a much improved sensitivity compared with the nanobelts alone. The authors suggest that the coated V_2O_5 nanobelts exhibit enhanced sensitivity owing to the synergy between electrical transport through the largely depleted nanobelts and the effective gas sensing on the high surface area MOS nanoparticles that inject electrons into the nanobelts. The V_2O_5 nanobelts were synthesized using a chemical process based on a mild hydrothermal reaction of 0.1 M ammonium metavanadate solution in dilute nitric acid, and the MOS nanoparticle coatings were fabricated from ferric nitrate, tetrabutyl titanate, and tin tetrachloride in ethanol, for depositing Fe_2O_3, TiO_2, and SnO_2, respectively. The sensing mechanism is clarified in Fig. 10.12 with a schematic drawing of a longitudinal cross section of nanobelts coated with MOS nanoparticles.

Upon exposure to ethanol, the electron-depleted surface layers in both the nanobelts and the nanoparticles are reduced because of the electron injection that accompanies the reaction of ethanol with the reactive adsorbed oxygen species. The authors believe that the boundaries between metal oxide grains on the V_2O_5 nanobelts dominate the sensor resistance.

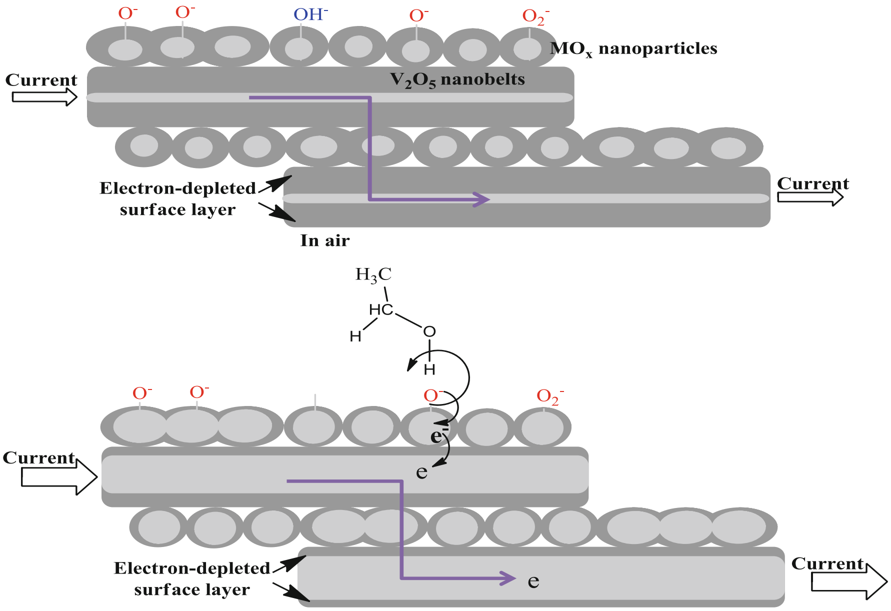


Fig. 10.12 Schematic of the ethanol-sensing mechanism of vanadium oxide sensors coated with SnO_2, TiO_2, and Fe_2O_3

As micromachined heater elements tend to be mechanically less sturdy than the ceramic substrate-based heaters in traditional gas sensors, we need to pay close attention to how the MOS nanoparticles are deposited. Techniques that do not exert mechanical pressure on the brittle micromachined heater substrates and result in porous nanoparticle films constitute the more attractive technologies. RF sputtering, for example, as used by Sadek et al. (2007), is a possible approach, but the process needs to be modified so as to generate more porous films.

As another example, Cukrov et al. (2001) synthesized tin oxide nanoparticles (average diameter 24 nm) and tested the O_2 sensing properties of porous thin films prepared by mechanochemical processing and spin coating. The mechanochemical process uses a conventional ball mill in which the mechanical energy activates the necessary chemical reactions and induces structural changes. These particles were subsequently spin coated in a thin film on alumina substrates with interdigitated electrodes (measuring electrodes on the front side and the heater on the back side). These films were tested for their oxygen-sensing potential and were found to be extremely stable and repeatable. Although the nanomaterial is very interesting because it does not require any metal catalyst and because of its demonstrated stability, spin coating is not a method of choice to coat the MOS on fragile microelectromechanical system (MEMS) or nanoelectromechanical system (NEMS) structures. Screen printing of electrodes and sensing materials, as often employed in the construction of traditional gas sensors, is an even less attractive candidate as significant pressure is exerted on the substrate in the silk screen printing (Fine et al. 2010). During screen printing, pressure is exerted on the structures, and therefore it may not be a very useful technique for fabricating fragile nanogas sensors (Viricelle et al. 2006).

Another nanopowder gas sensor, based on the synthesis of Al-doped TiO_2 nanoparticles (average diameter 100 nm), was reported by Choi et al. (2007). The nanopowder in this study was used to make thick-film gas sensors to measure CO selectively and sensitively in an O_2 environment. A thick film of this material was prepared on an alumina substrate with interdigitated Pt-measuring electrodes. To integrate the material with the measuring electrodes, the nanopowder was mixed in an appropriate solvent (alpha teripineol) and, drop by drop, was deposited on the electrodes followed by drying and densifying, at 100 °C and 800 °C, respectively, on the thus deposited films. This chemical method as well as sol-gel techniques and physical vapor deposition (Fine et al. 2010) are all feasible approaches to integrate sensing materials on brittle MEMS and NEMS structures. An especially attractive approach to deposit MOS locally on a brittle heater structure is to use the heat of the heater element itself to initiate the CVD from a metallo-organic precursor. Such an approach was pioneered by Cavicchi et al. (Sharma and Madou 2012), who deposited films on the prefabricated gas heater structures employing thermally activated CVD.

In CVD, a controlled mixture of precursors is brought in contact with a heated substrate, which causes a chemical reaction between the vapor and the substrate and leads to the deposition of a layer of the desired compound on the substrate. A basic outline of the CVD method is illustrated in Fig. 10.13.

Commonly employed CVD techniques include atmospheric pressure CVD (APCVD), aerosol-assisted CVD (AACVD), PECVD, and rapid thermal CVD. An advantage of using CVD for gas sensor purposes is that the thickness and density of the film can be optimized by controlling the concentration of the reagents in the vapor and the time of deposition. A concentrated vapor precursor yields a compact film that may grow at a rate of up to 1 $\mu m\,min^{-1}$; a rarified mixture of reagents on the other hand deposits a more porous film at a considerably lower growth rate (Fine et al. 2010).

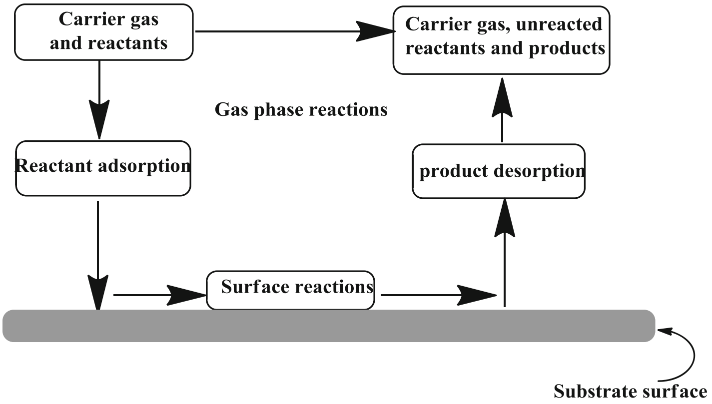


Fig. 10.13 Basic outline of the CVD technique

Two relevant CVD applications are by Shaw et al. and Ashraf et al. (Shaw et al. 2005; Ashraf et al. 2008). Shaw et al. employed AACVD for the deposition of tungsten oxide from W $(OPh)_6$ (the precursor) in toluene at 600 °C. After a deposition time of 90 min, a 50–75-nm-thick fibrous film was obtained. The thus fabricated films can be made thicker by using an electrical field in the CVD process. The authors investigated the porosity of the tungsten oxide films, a feature, as we know, of key importance for the utility of these films in gas sensing, at different applied voltages. Ashraf et al. demonstrated that APCVD is an effective technique for depositing tungsten films as thick as 3.6–6.7 mm. They used WCl6 as the precursor vapor and operated the reactor at 625 °C in N2. The particles in these up to 6.7-mm-thick tungsten oxide films were thin needle-like crystals with a high surface area and high porosity. Significantly, Ashraf et al. found that the MOS films deposited this way are more sensitive than those fabricated by screen printing.

Carbon nanotube (CNT)-based miniaturized gas sensors constitute yet another innovation in nanogas sensing. A single-walled CNT is a one-molecule-thick layer of graphite rolled into a cylinder with a diameter of a few nanometers. Multi-walled CNTs are composed of several such graphite cylinders rolled up into one. The distribution of electrons on their outer surface only makes CNTs extremely sensitive to charge transfer and chemical doping effects by surrounding molecules (Zhang et al. 2008). When electron-withdrawing or electron-donating gas molecules come in contact with CNTs, it very dramatically changes the surface electron concentration. CNT-based gas sensors show faster response, higher sensitivity, and lower operating temperatures and detection ability for a wider variety of gases than any other gas-sensitive materials (Suehiro et al. 2003). Because of these extensively perceived advantages, the use of CNTs, both pristine and functionalized, continues to be studied extensively. Unfortunately, the difficulty in making electrical contact to CNTs and the tremendous variety of lengths, thicknesses, and conductivities they come in have hampered progress. Our approach to nanogas sensing with suspended CNWs (§5) constitutes a viable alternative to CNT-based gas sensing as we can control contact resistance, thickness, and resistivity of the nanowires very well.

Gas-Sensing Characteristics of Metal Oxides

(A) Sensitivity

It is the response of a gas sensor per unit change in the gas concentration. Since metal oxide gas sensors are based on the principle of chemiresistivity, it is generally defined in terms of conductance or resistance. For n-type material in the presence of reducing gas and p-type material in the presence of oxidizing gas, sensitivity can be defined as:

$$S = \left(R_a - R_g\right)/R_g$$

where R_a and R_g are the stable values of the resistance of the material before and after exposure to gas.

(B) Selectivity

A sensor should respond to only a particular molecule in a mixture of environment. The selectivity of a gas sensor toward a particular molecule is the ratio of its response toward it and that of another dominant interfering molecule in the atmosphere.

$$\text{Selectivity of an gas sensor} = \frac{\text{sensitivity of particular molecule}}{\text{sensitivity towards an interferrent}}$$

Selectivity of a gas sensor should be always greater than one.

(C) Accuracy

Accuracy represents the degree of exactness of a measurement compared to the true value.

(D) Speed of Response

The time required for a sensor to reach 90% of the total response of the signal such as resistance upon exposure to the target gas.

(E) Recovery Time

The time required for a sensor to return to 90% of the original baseline signal upon removal of target gas.

(F) Detection Limit

It is the lowest concentration of the gas that can be detected under given conditions, particularly at a given temperature.

(G) Precision

It is a measure of repeatability of a gas sensor.

(H) Error

It is the difference between the measurand value and true value.

(I) Dynamic Range

The concentration range between the detection limit and the upper limiting concentration.

(J) Linearity

The relative deviation of an experimentally determined calibration graph from an ideal straight line. Usually values for linearity are specified for a definite concentration range.

(K) Resolution

The lowest concentration difference which can be distinguished when the composition is varied continuously. This parameter is important chiefly for detectors in flowing streams.

Table 10.1 Comparison of various types of gas sensors

Parameters	Kinds of gas sensors				
	SMO	Electrochemical	Catalytic combustion	Thermal conductivity	Infrared absorption
Sensitivity	H	G	G	L	H
Selectivity	M	G	L	L	H
Response time	H	M	G	G	L
Durability	G	M	G	G	H
Accuracy	G	G	G	G	H
Stability	G	L	G	G	G
Suitability to portable instruments	H	M	G	G	L

H high, *G* good, *M* moderate, *L* low

(L) **Stability**

The ability of the sensor to maintain its performance for a certain period of time. As a measure of stability, drift values are used, e.g., the signal variation for zero concentration.

(M) **Life Cycle**

The length of time over which the sensor will operate. The maximum storage time (shelf life) must be distinguished from the maximum operating life. The latter can be specified either for continuous operation or for repeated on-off cycles (Jimenez-Cadena et al. 2007; Korotcenkov 2007a, b; Wang et al. 2010).

Table 10.1 is summarizing the comparison of various kinds of the mentioned gas sensors and its most proper parameters that have been studied by Korotcenkov (2007a, b).

10.3 Applications of Gas Sensors

While the previous sections focused on the scientific breakthroughs achieved by constantly pushing the fundaments of sensing materials and devices, focus in the following is addressed toward the applicative aspects of chemoresistive gas sensors.

Rapid, comprehensive, and reliable information regarding the chemical state of a gaseous system is currently indispensable in many high-technology fields. Solid-state gas sensors are thus generating tremendous interest because of their widespread applications in industry, environmental monitoring, space exploration, biomedicine, and pharmaceutics. Generally, basic criteria for these practical gas-sensing devices are (i) high sensitivity and selectivity; (ii) fast response time and recovery time; (iii) low power consumption; (iv) low operating temperature and temperature independence; and (v) high stability (Hung et al. 2017).

For most of the practical applications, a relevant problem is not only to estimate the target gas concentration but also to identify it in the real mixture (outdoor and indoor ambient, exhaust gases, breath). Unfortunately, chemoresistive gas sensors are very sensitive but not selective. Such a task can therefore not be performed by a single sensor. E-nose, an artificial olfactory system consisting of an array of sensors, then needs to be used. Each sensor shows an individual response to all (or to a certain subset) of the target gases which are identified by pattern recognition of the sensor signals, e.g., that developed by Cyrano Sciences is based on the concept of using multiple semi-selective sensors combined with electronic computation, first proposed by Gardner and Bartlett (Wilson and Baietto 2009).

In the following, some of the most important applicative fields of semiconductor gas sensors are listed.

10.3.1 Environmental Applications

In environmental applications, field-portable monitors based on chemoresistive sensor devices are particularly suited to comply with the newly reinforced environmental regulations and give a valuable alternative to conventional analytical techniques; they are accurate but more expensive and time-consuming (Yamazoe and Miura 1994). Metal oxide semiconductor sensors are relatively inexpensive compared to other sensing technologies; they are also robust, lightweight, and long-lasting and benefit from high material sensitivity and quick response times. These properties could lead them to becoming ever more important tools in environmental monitoring with respect to the other type of sensors. They can be used to measure and monitor trace amounts of environmentally important gases such as carbon monoxide and nitrogen dioxide (Fine et al. 2010). Today, it is also highly desirable to develop simple and inexpensive sensors to measure atmospheric carbon dioxide in order to monitor indoor air quality (Marsal et al. 2003).

10.3.2 Automotive Applications

The ability of chemosensors based on refractory metal oxides to withstand high temperatures, the robust nature, efficient packaging procedures, and small size are strong technical merits for automotive applications. Indeed, usually high temperatures are reached in the exhausts, and sensor devices should operate in the range 600–900 °C in a harsh ambient requiring advanced packaging. Another requirement for these sensors is reaction measurement speed of the order of fraction of seconds and 5–10-year service life. As a result of the introduction of emergent technologies in the automotive industry, new vehicle diagnostic sensors are at present necessary to control motor functioning, monitor a range of emission gases (NO, NO_2, CO, CO_2, HC, O_2, etc.), and detect high pollution levels in the vehicle cabin (Pijolat et al. 1999).

Chemoresistive sensors can be used to minimize the emission of CO, hydrocarbons, and nitrogen oxides coming from combustion engines. It is important for the engine to operate with the proper air-to-fuel ratio (A/F) so that combustion parameters are optimized. The first titania gas sensors were developed in the late 1970s and early 1980s. They were primarily used to detect the stoichiometric A/F (Cederquist et al. 1976). In these instances, the sensor resistance increased by orders of magnitude around the stoichiometric A/F, making it a very useful device for these applications.

Chemoresistive sensors will have high importance also in future cars. In fact, CO sensors have been identified as a critical need for proton exchange membrane (PEM) fuel cell systems, which offer a viable approach to improve efficiency of power generation from fossil fuels, while reducing emissions of pollutants and greenhouse gases (Holt et al. 2002). The primary uses of such sensors include measurement of the CO content of the reformate gas entering the PEM fuel cell (i.e., for fuel cell protection) and measurement of the CO content of the reformate gas at various catalytic stages of the fuel processor (for fuel processor feedback and control). A further requirement is that these sensors must not exhibit cross sensitivities to the gaseous components of the reformed gases (e.g., hydrogen, carbon dioxide, and/or humidity) or to other potential contaminants.

10.3.3 Biomedical Applications

Biomedical uses of chemoresistive gas sensors (e.g., in breath test) require instead high sensitivity to detect very low concentrations of target gases (in the ppt-ppm range), coming from biochemical processes occurring in the human body and used as markers for several pathologies (152 D'Amico et al. 2008). Furthermore, the target gas is to be analyzed and quantified in a complex mixture, i.e., in the presence of many other interferent gases and a high humidity content. Such sensors can complement or serve as an alternative to more sophisticated spectrometric systems for breath analysis and speciation, especially for clinical diagnostics and monitoring (Righettoni et al. 2015).

10.3.4 Health-Care Application

In the human gas breath, detection technique can be obtained; decreasing the cost of the system is essential for the spread of the breath-analyzing system. Sensor device or a detector that aimed to a high-performance breath gas detector at the medical diagnosis level was developed by Ohsawa et al. (2007).

The main gas composition of human breath consists of the following gases:

(i) Nitrogen that is the most common gas in atmosphere
(ii) Carbon dioxide produced by respiration

Table 10.2 Comparison of various types of gas sensors

Type of gas	Name of gas	Chemical formula	Relation to physical condition	
Reducing	Hydrogen	H_2	Abnormality of intestinal anaerobes	Semiconductor (ppm)
	Methane	CH_4	Abnormality of intestinal anaerobes	
	Carbon monoxide	CO	Smoking and oxidation stress	ElectroChem. (ppm)
	Ethanol	C_2H_5OH	Drinking	
	Acetone	CH_3COCH_3	Diabetes, obesity, and dieting	Semiconductor (ppm)
	Hydrogen peroxide	H_2O_2	Smoking	
	Isoprene	C_5H_8	Cholesterol synthesis intermediates	
Sulfur	Hydrogen sulfide	H_2S	Periodontitis	GC/MS(ppb)
	Methyl mercaptan	CH_3SH	Periodontitis, liver disease, colon cancer	
Amine	Ammonia	NH_3	Hepatitis, *H. Pylori* test	Semiconductor (ppm)
VOC	Nonanaldehyde	$C_9H_{18}O$	Lung cancer	GC/MS(ppb)
	Benzene	C_6H_6		

(iii) Water vapor generated from bodily fluids
(iv) Oxygen that was not consumed

Table 10.2 is a summary of the sensing methods and the relationships between the physical conditions or diseases and various biogases (Shin et al. 2015).

For such analysis or health screening, technologies are necessary to selectively detect various gas compounds in the breath and to measure the concentration of important gas species that are correlated with halitosis, metabolism, and disease (Shin et al. 2011).

Recently, the capacities to monitor health conditions and to predict disease noninvasively became easy without infringing the Medical Practitioners Act. One of the simple ways of detection is to make predictions based on biogas, just as in the previous times when the physicians made decisions by smelling the odor from patients. A representative example is alcohol detection tool in the breath, which will be nearly commercially available. However, drunkenness is caused by an external factor, and it is not an index of a human state. Also, there are devices of urea breath test to detect carbamide peroxide and other devices used for asthma patients to measure nitric oxide (Itoh et al. 2013).

Research is being conducted actively to clarify the relationships between various diseases and breath components, such as monitoring the liver function using ammonia, evaluation of cholesterol metabolism by isoprene, and monitoring the blood carboxyhemoglobin by carbon monoxide (Shin et al. 2015).

10.3.5 Miscellaneous Applications

During recent years, single or array of metal oxide semiconductor (MOS) sensors have found applications in many other different fields than those listed above, including odor landfill, chemical agent warfare detection, food quality control, etc. (Casalinuovo and Pierro 2006). These technologies enable rapid detection and identification of substances based on their chemical profile. They find applications in the monitoring of some medical conditions as well as industrial applications generally related to quality control or contamination detection. A new multichamber electronic nose (MCE-nose) which overcomes, to a great extent, one of the major disadvantages of the use of MOS technology for e-noses – the long recovery period needed after each gas exposure that severely restricts its use in applications where the gas concentrations may change rapidly – has been also proposed (G-Jimenez et al. 2011). It comprises several identical sets of MOS sensors accommodated in separate chambers which alternate between sensing and recovery states, providing, as a whole, a device capable of sensing more quickly changes in chemical concentrations.

10.3.6 New Opportunities

Although resistive gas sensors are still commercialized intensively as bulk devices, there is a strong demand for novel, smaller, integrated, high-performance, and reliable devices for advanced applications. Technological advances will assist gas sensor device scale of economies by exploring more efficient fabrication methods that may include material and component assembly into the final device.

At the material level, technological advances will arise from multidisciplinary contributions, which will hopefully open up new areas of nanoscience research. In the past few years, large efforts have been expended in the development of new synthetic approaches for sensing materials at the nanoscale. Advances in recent activities concerning the synthesis, characterization, and properties of novel materials with potential in sensing applications can be found in many reviews (Neri 2011; Carbone and Cozzoli 2010). Among the obvious challenges are improving reproducibly and control over nanoparticle structure, surface chemistry, and dispersion.

Future work will continue to focus also on generating improved component assembly and device fabrication strategies. For small- or medium-scale batch production, a hybrid design whereby component parts are created separately for subsequent assembly into a complete system is an attractive option, as it removes many of the restrictions imposed by the need for process compatibility.

Integrated gas sensor with a microhotplate (MHP) demonstrates better sensitivity, faster response, and lower power consumption than traditional thick-film devices. For the detection of a target gas, a gas-sensitive layer is applied on a suspended microhotplate that is mounted on top of a silicon chip. Any gas-induced change of the gas-sensitive layer's surface potential is detected and digitally processed by the integrated electronics.

Sensor platforms robust enough for integration into standard, industrial weaving processes have been proposed (Ataman et al. 2013). Such sensors were fabricated on a thin, flexible plastic stripe and woven into a cotton fabric by using a standard weaving machine, to create a smart fabric able to detect ambient gas. The fabrication process is actually very simple and compatible with large-scale roll-to-roll fabrication. Inkjet printing can be used as an effective, low-cost alternative, suitable for the fabrication of long sensor stripes. Bending tests performed on the devices showed that they can be successfully woven within a cotton fabric using a standard weaving machine without being damaged.

From a processing point of view, employing modern microelectronics technology to manufacture both the sensing element and the signal conditioning circuitry on a single silicon chip is now possible to make low-power, low-cost smart gas sensors in high volume, and this should result in a new generation of miniaturized gas sensors (Gardner et al. 2010). Full integration of microelectronic and micro-mechanical components on a single wafer has been achieved commercially using silicon processing technology.

The sensing element is comprised of a sensing chip and an integrated heater fabricated on a silicon substrate using MEMS technology and a metal oxide semiconductor layer on the sensing chip. Due to miniaturization of the sensing chip, the sensor requires a heater power consumption of only 15 mW and is suitable for low-power equipment and battery-operated instruments. We expect many areas will benefit from these miniaturized sensors, including transportation (land, sea, air, and space), buildings and facilities (homes, offices, and factories), humans (especially for health and medical monitoring), and robotics of all types.

Recent technological advances are quickly changing the landscape of gas sensors. As these devices are becoming smaller in size, require less support infrastructure than currently used equipment, and are capable of operating autonomously, new opportunity for gas sensors could come from their integration into smartphones [86]. Chemical sensors, integrated within smartphones and other wireless and wearable devices, provide a vast array of functionality, from informing people about their conditions through breath analysis. For example, background apps on a smartphone can monitor CO or CO_2 levels and provide safe/warning/alert indication to the user about possible dangerous changes in their environment.

Furthermore, monitoring devices can become simpler and cheaper as the computation is pushed to the cloud. This enables users to buy off-the-shelf devices and access customized monitoring applications via cloud-based services.

10.4 Conclusions

In this study, the historical progress of semiconductor gas sensors carried out during the past century has been briefly reviewed. As it follows from conducted analysis, the choice of an appropriate material for gas sensors should be based on good gas response time, high selectivity, low sensitivity to air humidity, low hysteresis, thermal cycling, high stability of parameters over the time, all range of operation temperatures, and on exposure to the various chemicals likely to be present in the environment. Therefore required efficiency of reactions, responsible for gas sensors' sensitivity, is necessary to achieve, taking into account the necessity of an attainment of maximum chemical, structural, and long-term stability of the device's parameters.

Such requirements drive the trends of R&D in gas sensors industry, which in turn fuels opportunities for technology progress that can open up new applications of gas sensors. Whereas many different approaches to gas detection are available, the R&D of solid-state gas sensors has extremely developed in recent years. Due to the diversity of solid-state gas sensors, it's impossible to deal with all the different types of solid-state gas sensors. Hence, herewith we focused on the basics of some of the main solid-state gas sensors, discussing the principles of operation for each and the future trends of the scientific research. In particular, metal oxide gas sensors were discussed in more detailed with respect to the other types of solid-state gas sensors due to their comparative simplicity, low cost, and advantages that should work in their favor as new types of applications and technologies emerge.

In the next few days, there is no doubt that nanostructured metal oxides will constitute the key for the development of semiconducting gas sensors with improved gas-sensing properties. Not only in chemical gas sensors but also in solid-state gas sensors nanocrystalline materials will play a fundamental role in the gas sensors of new generation. In fact, nanoscience and nanotechnology are dedicating great efforts to developing of novel materials for gas sensor applications. This new classification of nanostructures shows a great potential for applications in ultrasmall sensors because the conductivity of these materials changes dramatically when gas or liquid molecules attach their surfaces. In addition, with the development of standard wireless communication protocols optimized for sensors, wireless sensor network is expected to gain a wide approval in applications such as homeland security, process monitoring, food monitoring, and medical instrumentation.

Creation of new sensitive, selective, and stable gas sensor materials is one of the most important and actual tasks of nanotechnology.

Acknowledgement The authors wish to thank Dr. Aya Gomaa for technical assistance.

References

Acquaroli LN, Urteaga R, Koropecki RR (2010) Innovative design for optical porous silicon gas sensor. Sensors Actuators B Chem 149:189–193. https://doi.org/10.1016/j.snb.2010.05.065

Aleixandre M, Gerboles M (2012) Review of small commercial sensors for indicative monitoring of ambient gas. Chem Eng Trans 30:169–174. http://publications.jrc.ec.europa.eu/repository/handle/JRC75718

Anisimkin VI, Penza M, Valentini A, Quaranta F, Vasanelli L (1995) Detection of combustible gases by means of a ZnO-on-Si surface acoustic wave (SAW) delay line. Sensors Actuators B Chem 23:197–201. https://doi.org/10.1016/0925-4005(94)01273-K

Anuradha S, Rajanna K (2006) Development of thermoelectric gas sensors for volatile organic compounds. In: Proceedings of the 5th IEEE conference on sensors, Daegu, pp 716–718. https://doi.org/10.1109/ICSENS.2007.355561

Arshak K, Moore E, Lyons GM, Harris J, Clifford S (2004) A review of gas sensors employed in electronic nose applications. Sens Rev 24:181–198. https://doi.org/10.1108/02602280410525977

Ashraf S, Blackman CS, Naisbitt SC, Parkin IP (2008) The gas sensing properties WO_{3-x} thin films deposited via the atmospheric pressure chemical vapor deposition (APCVD) of WCl6 with ethanol. Meas Sci Technol 19:025203. https://doi.org/10.1088/0957-0233/19/2/025203

Ataman C, Kinkeldei T, Mattana G, V-Quintero A, Molina-Lopez F, Courbat J, Cherenack K, Briand D, Tröster G, de Rooij NF (2013) A robust platform for textile integrated gas sensors. Sensors Actuators B Chem 177:1053–1061. https://doi.org/10.1016/j.snb.2012.11.099

Azad AM, Akbar SA, Mhaisalkar SG, Birkefeld LD, Goto KS (1992) Solid-state gas sensors: a review. J Electrochem Soc 139:3690–3704. https://doi.org/10.1149/1.2069145

Barsan N, Weimar U (2001) Conduction model of metal oxide gas sensor. J Electroceram 7:143–167. https://doi.org/10.1023/A:1014405811371

Bârsan N, Weimar U (2003) Understanding the fundamental principles of metal oxide based gas sensors; the example of CO sensing with SnO_2 sensors in the presence of humidity. J Phys Condens Matter 15:813–839. https://doi.org/10.1088/0953-8984/15/20/201

Barsan N, Schweizer-Berberich M, Göpel W (1999) Fundamental and practical aspects in the design of nanoscaled SnO_2 gas sensors: a status report. Fresenius J Anal Chem 365:287–304. https://doi.org/10.1007/s002160051490

Beck K, Kunzelmann T, Von Schickfus M, Hunklinger S (1999) Contactless surface acoustic wave gas sensor. Sensors Actuators A 76:103–106. https://doi.org/10.1016/S0924-4247(98)00359-8

Becker T, Ahlers S, Bosch V, Braunmuhl C, Muller G, Kiesewetter O (2001) Gas sensing properties of thin-and thick-film tin-oxide materials. Sensors Actuators B Chem 77:55–61. https://doi.org/10.1016/S0925-4005(01)00672-4

Brattain WH, Bardeen J (1952) Surface properties of germanium. Bell Syst Tech J 32:1–41. https://doi.org/10.1002/j.1538-7305.1953.tb01420.x

Cabot A, Arbiol J, Morante JR, Weimar U, Barsan N, Gopel W (2000) Analysis of the noble metal catalytic additives introduced by impregnation of as obtained SnO_2 sol-gel nanocrystals for gas sensors. Sensors Actuators B Chem 70:87–100. https://doi.org/10.1016/S0925-4005(00)00565-7

Carbone L, Cozzoli PD (2010) Colloidal heterostructured nanocrystals: synthesis and growth mechanisms. Nano Today 5:449–493. https://doi.org/10.1016/j.nantod.2010.08.006

Casalinuovo I, Pierro D (2006) Application of electronic noses for disease diagnosis and food spoilage detection. Sensors 6:1428–1439. https://doi.org/10.3390/s6111428

Cederquist A, Gibbons E, Meitzler A (1976) Characterization of Zirconia and Titania engine exhaust gas sensors for air/fuel feedback control systems. SAE Tech Pap. https://doi.org/10.4271/760202

Chao Y, Yao S, Buttner WJ, Stetter JR (2005) Amperometric sensor for selective and stable hydrogen measurement. Sensors Actuators B Chem 106:784–790. https://doi.org/10.1016/j.snb.2004.09.042

Chen D, Liu W, Zhang Y, Liu J, Kan R, Wang M, Chen J, Cui Y (2006a) H_2S detection by tunable diode laser absorption spectroscopy. In: Proceedings of the IEEE international conference on information acquisition, Shandong, 20–23 August, pp 754–758. https://doi.org/10.1109/ICIA.2006.305823

Chen H, Liu X, Muthuraman H, Zou J, Wang J, Dai Q (2006b) Direct laser writing of microtunnels and reservoirs on nanocomposite materials. Adv Mater 18:2876–2879. https://doi.org/10.1002/adma.200601560

Chen X, Wong CKY, Yuan CA, Zhang G (2013) Nanowire-based gas sensors. Sensors Actuators B Chem 177:178–195. https://doi.org/10.1016/j.snb.2012.10.134

Choi YJ, Seeley Z, Bandyopadhyay A, Bose S, Akbar SA (2007) Aluminum-doped TiO_2 nanopowders for gas sensors. Sensors Actuators B Chem 124:111–117. https://doi.org/10.1016/j.snb.2006.12.005

Comini E (2006) Metal oxide nano-crystals for gas sensing. Anal Chim Acta 568:28–40. https://doi.org/10.1016/j.aca.2005.10.069

Comini E, Faglia G, Sberveglieri G (2002) Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts. Appl Phys Lett 81:1869–1871. https://doi.org/10.1063/1.1504867

Cukrov LM, McCormick PG, Galatsis K, Wlodarski W (2001) Gas sensing properties of nanosized tin oxide synthesized by mechanochemical processing. Sensors Actuators B Chem 77:491–495. https://doi.org/10.1016/S0925-4005(01)00751-1

Currie JF, Essalik A, Marusic J-C (1999) Micromachined thin film solid state electrochemical CO_2, NO_2 and SO_2 gas sensors. Sensors Actuators B 59:235–241. https://doi.org/10.1016/S0925-4005(99)00227-0

D'Amico A, di Natale C, Paolesse R, Macagnano A, Martinelli E, Pennazza G, Santonico M, Bernabei M, Roscioni C, Galluccio G, Bono R, Agrò EF, Rullo S (2008) Olfactory systems for medical applications. Sensors Actuators B Chem 130:458–465. https://doi.org/10.1016/j.snb.2007.09.044

de Graaf G, Wolffenbuttel R (2012) Surface-micromachined thermal conductivity detectors for gas sensing. In: Proceedings of the IEEE international instrumentation and measurement technology conference (I2MTC), Graz, 13–16 May, pp 1861–1864. https://doi.org/10.1109/I2MTC.2012.6229412

Dey A (2018) Semiconductor metal oxide gas sensors: a review. Mater Sci Eng B 229:206–217. https://doi.org/10.1016/j.mseb.2017.12.036

Dolbec R, el Khakani MA, Serventi AM, Saint-Jacques RG (2003) Influence of the nanostructural characteristics on the gas sensing properties of pulsed laser deposited tin oxide thin films. Sensors Actuators B Chem 93:566–571. https://doi.org/10.1016/S0925-4005(03)00229-6

Dutta A, Nishiguchi H, Takita Y, Ishihara T (2005) Amperometric hydrocarbon sensor using La(Sr)Ga(Fe)O_3 solid electrolyte for monitoring in exhaust gas. Sensors Actuators B Chem 108:368–373. https://doi.org/10.1016/j.snb.2004.10.042

El Kady M, Shokry H, Hamad H (2016) Effect of superparamagnetic nanoparticles on the physicochemical properties of nano hydroxyapatite for groundwater treatment: adsorption mechanism of Fe(II) and Mn(II). RSC Adv 85:82244–82259. https://doi.org/10.1039/c6ra14497g

El-Aassar MR, El-Kady MF, Hassan HS, Al-Deyab SS (2016) Synthesis and characterization of surface modified electrospun poly (acrylonitrile-co-styrene) nanofibers for dye decolorization. J Taiwan Inst Chem Eng 58:274–282. https://doi.org/10.1016/j.jtice.2015.05.042

Elkady MF, Hassan HS (2015) Equilibrium and dynamic profiles of azo dye sorption onto innovative nano-zinc oxide biocomposite. Curr Nanosci 11:805–814. https://doi.org/10.2174/1573413711666150415003115

Fine GF, Cavanagh LM, Afonja A, Binions R (2010) Metal oxide semiconductor gas sensors in environmental monitoring. Sensors 10:5469–5502. https://doi.org/10.3390/s100605469

Firth JG, Jones A, Jones T (1973) The principles of the detection of flammable atmospheres by catalytic devices. Combust Flame 20:303–311. https://doi.org/10.1016/0010-2180(73)90021-7

Fischerauer G, Dickert F, Forth P, Knauer U (1996) Chemical sensors based on SAW resonators working at up to 1 GHz. In: Proceedings of the IEEE ultrasonics symposium, 1:439–442. https://doi.org/10.1109/ULTSYM.1996.584007

Font X, Artola A, Sánchez A (2011) Detection, composition and treatment of volatile organic compounds from waste treatment plants. Sensors 11:4043–4059. https://doi.org/10.3390/s110404043

Gan T, Hu S (2011) Electrochemical sensors based on graphene materials. Microchim Acta 175:1–19. https://doi.org/10.1007/s00604-011-0639-7

Garcia-R D, Martínez A, Azcona C (2012) NDIR-based CO_2 monitor system for wireless sensor networks, IEEE Latin American symposium on circuits and systems LASCAS, Playa Del Carmen, 29 February–2 March, 1–4. https://doi.org/10.1109/LASCAS.2012.6180326

Gardner JW, Guha PK, Udrea F, Covington JA (2010) CMOS interfacing for integrated gas sensors: a review. IEEE Sensors J 10:1833–1848. https://doi.org/10.1109/JSEN.2010.2046409

Girschikofsky M, Rosenberger M, Belle S, Brutschy M, Waldvogel SR, Hellmann R (2012) Optical planar Bragg grating sensor for real-time detection of benzene, toluene and xylene in solvent vapour. Sensors Actuators B Chem 171–172:338–342. https://doi.org/10.1016/j.snb.2012.04.046

Gonzalez-Jimenez J, Monroy JG, Blanco JL (2011) The multi-chamber electronic nose-an improved olfaction sensor for mobile robotics. Sensors 11:6145–6164. https://doi.org/10.3390/s110606145

Gopel W, Schierbaum K (1995) SnO_2 sensors: current status and future prospects. Sensors Actuators B Chem 26/27:1–12. https://doi.org/10.1016/0925-4005(94)01546-T

Gurlo A, Riedel R (2007) In situ operando spectroscopy for assessing mechanisms of gas sensing. Angew Chem Int Ed 46:3826–3848. https://doi.org/10.1002/anie.200602597

Halek G, Malewicz M, Teterycz H (2009) Methods of selectivity improvements of semiconductor gas sensors. In: Proceedings of the international students and young scientists workshop on photonics and microsystem', Wernigerode, 25–27 June, pp 31–35. https://doi.org/10.1109/STYSW.2009.5470313

Hassan SH, Kashyout AB, Soliman HMA, Uosif MA, Afify N (2013) Effect of reaction time and Sb doping ratios on the architecturing of ZnO nanomaterials for gas sensor applications. Appl Surf Sci 277:73–82. https://doi.org/10.1016/j.bjbas.2014.10.007

Hassan SH, Kashyout AB, Morsi I, Nasser AAA, Ali I (2014a) Synthesis, characterization and fabrication of gas sensor devices using ZnO and ZnO: in nanomaterials. J Basic Appl Sci 3:216–221. https://doi.org/10.1016/j.bjbas.2014.10.007

Hassan SH, Kashyout AB, Morsi I, Nasser AAA, Raafat A (2014b) Fabrication and characterization of gas sensor micro-arrays. Sens Bio-Sens Res 1:34–40. https://doi.org/10.1016/j.sbsr.2014.04.001

Hassan SH, Kashyout AB, Morsi I, Nasser AAA, Raafat A (2014c) Fabrication and characterization of nano-gas sensor arrays. AIP Conf Proc 1:34–40. https://doi.org/10.1063/1.4914233

Hassan SH, Kashyout AB, Morsi I, Nasser AAA, Abuklill H (2015) Development of polypyrrole coated copper nanowires for gas sensor application. Sens Bio-Sens Res 5:50–54. https://doi.org/10.1016/j.sbsr.2015.07.004

Heiland G (1957) Zum einfluss von wasserstoff auf die elektrische leitfähigkeit von Zinkoxydkristallen. Z Phys 138:459–464. https://doi.org/10.1007/BF01327362

Ho K-C, Hung W-T (2001) An amperometric NO_2 gas sensor based on Pt/ Nafion® electrode. Sensors Actuators B Chem 79:11–16. https://doi.org/10.1016/S0925-4005(01)00782-1

Holt CT, Azad A-M, Swartz SL, Rao RR, Dutta PK (2002) Carbon monoxide sensor for PEM fuel cell systems. Sensors Actuators B Chem 87:414–420. https://doi.org/10.1016/S0925-4005(02)00290-3

Huang X-J, Choi Y-K (2007) Chemical sensors based on nanostructured materials. Sensors Actuators B Chem 122:659–671. https://doi.org/10.1016/j.snb.2006.06.022

Huang J, Wan Q (2009) Gas sensors based on semiconducting metal oxide one-dimensional nanostructures. Sensors 9:9903–9924. https://doi.org/10.3390/s91209903

Hübert T, Boon-Brett L, Black G, Banach U (2011) Hydrogen sensors –a review. Sensors Actuators B Chem 157:329–352. https://doi.org/10.1016/j.snb.2011.04.070

Hung CM, Le DTT, Hieu NV (2017) On-chip growth of semiconductor metal oxide nanowires for gas sensors: a review. J Sci 2:263–285. https://doi.org/10.1016/j.jsamd.2017.07.009

Itoh T, Nakashima T, Akamatsu T, Izu N, Shin W (2013) Nonanal gas sensing properties of platinum, palladium, and gold-loaded tin oxide VOCs sensors. Sensors Actuators B Chem 187:135–141. https://doi.org/10.1016/j.snb.2012.09.097

Jiang T, Wang Z, Li Z, Wang W, Xu X, Liu X, Wang J, Wang C (2013) Synergic effect within n-type inorganic–p-type organic nano-hybrids in gas sensors. J Mater Chem C 1:3017–3025. https://doi.org/10.1039/C3TC00370A

Jimenez-Cadena G, Riu J, Xavier Rius F (2007) Gas sensors based on nanostructured materials. Analyst 132:1083–1099. https://doi.org/10.1039/b704562j

Karthikeyan S, Pandya HM, Sharma MU, Gopal K (2015) Gas sensors-a review. J Environ Nanotechnol 4:1–14. https://doi.org/10.13074/jent.2015.12.153163

Kasai N, Tsuchiya C, Fukuda T, Sekine K, Sano T, Takehana T (2011) Propane gas leak detection by infrared absorption using carbon infrared emitter and infrared camera. NDT E Int 44:57–60. https://doi.org/10.1016/j.ndteint.2010.09.006

Kashyout AB, Soliman HMA, Hassan SH, Abousehly AM (2010) Fabrication of ZnO and ZnO:Sb nanoparticles for gas sensor applications. J Nanomater 2010:1–8. https://doi.org/10.1155/2010/341841

Khodadadi A, Mohajerzadeh SS, Mortazavi Y, Miri AM (2001) Cerium oxide / SnO_2-based semiconductor gas sensors with improved sensitivity to CO. Sensors Actuators B Chem 80:267–271. https://doi.org/10.1016/S0925-4005(01)00915-7

Kim H-J, Lee J-H (2014) Highly sensitive and selective gas sensors using p-type oxide semiconductors: overview. Sensors Actuators B Chem 192:607–627. https://doi.org/10.1016/j.snb.2013.11.005

Kim Y-J, Park SC, Yoon S, Ch L (2009) A micro-thermoelectric gas sensor for the detection of hydrogen and atomic oxygen. Analyst 134:236–242. https://doi.org/10.1039/B807882C

King WH (1964) Piezoelectric sorption detector. Anal Chem:1735–1739. https://doi.org/10.1021/ac60215a012

Kong J, Franklin NR, Zhou C, Chapline MG, Peng S, Cho K, Dai H (2000) Nanotube molecular wires as chemical sensors. Science 287:622–625. https://doi.org/10.1126/science.287.5453.622

Konishi R (1997) The concentration-estimation of inflammable gases with a semiconductor gas sensor utilizing neural networks and fuzzy inference. Sensors Actuators B Chem 41:121–129. https://doi.org/10.1016/S0925-4005(97)80284-5

Korotcenkov G (2005) Gas response control through structural and chemical modification of metal oxide films: state of the art and approaches. Sensors Actuators B Chem 107:209–232. https://doi.org/10.1016/j.snb.2004.10.006

Korotcenkov G (2007a) Practical aspects in design of oneelectrode semiconductor gas sensors: status report. Sensors Actuators B Chem 121:664–678. https://doi.org/10.1016/j.snb.2006.04.092

Korotcenkov G (2007b) Metal oxides for solid-state gas sensors: what determines our choice? Mater Sci Eng B 139:1–23. https://doi.org/10.1016/j.mseb.2007.01.044

Korotcenkov G (2008) The role of morphology and crystallographic structure of metal oxides in response of conductometric-type gas sensors. Mater Sci Eng B 61:1–39. https://doi.org/10.1016/j.mser.2008.02.001

Korotcenkov G, Cho B (2010) Grain size effect in structural stability of SnO_2 and In_2O_3 films aimed for gas sensing application. In: Proceedings of 2nd international conference on computer research and development, Kuala Lumpur, Malaysia, 7–10 May, pp 461–464. https://doi.org/10.1109/ICCRD.2010.100

La D-D, Kim CK, Jun TS, Jung Y, Seong GH, Choo J, Kim YS (2011) Pt nanoparticle-supported multiwall carbon nanotube electrodes for amperometric hydrogen detection. Sensors Actuators B Chem 155:191–198. https://doi.org/10.1016/j.snb.2010.11.045

Law M, Kind H, Messer B, Kim F, Yang PD (2002) Photochemical sensing of NO_2 with SnO_2 nanoribbon nanosensors at room temperature. Angew Chem Int Ed 41:2405–2408. https://doi.org/10.1002/1521-3757(20020703)114:13<2511::AID-ANGE2511>3.0.CO;2-N

Leblanc E, Perier-Camby L, Thomas G, Gibert R, Primet M, Gelin P (2000) NO_x adsorption onto dehydroxylated or hydroxylated tin dioxide surface. Application to SnO_2-based sensors. Sensors Actuators B Chem 62:67–72. https://doi.org/10.1016/S0925-4005(99)00376-7

Lee J-H (2009) Gas sensors using hierarchical and hollow oxide nanostructures: overview. Sensors Actuators B Chem 140:319–336. https://doi.org/10.1016/j.snb.2009.04.026

Lee H, Han D, Ahn H (1997) Design and fabrication of SAW gas sensor with resonator structure. In: Proceedings of the 5th international conference on properties and applications of dielectric materials, Seoul, 25–30 May, vol 2, pp 1058–1061. https://doi.org/10.1109/ICPADM.1997.616629

Lee SW, Tsai PP, Chen H (2000) Comparison study of SnO_2 thin and thick film gas sensors. Sensors Actuators B Chem 67:122–127. https://doi.org/10.1016/S0925-4005(00)00390-7

Lee C, Akbar SA, Park CO (2001) Potentiometric CO_2 gas sensor with lithium phosphorous oxynitride electrolyte. Sensors Actuators B Chem 80:234–242. https://doi.org/10.1016/S0925-4005(01)00902-9

Lee YC, Huang H, Tan OK, Tse MS (2008) Semiconductor gas sensor based on Pddoped SnO_2 nanorod thin films. Sensors Actuators B Chem 132:239–242. https://doi.org/10.1016/j.snb.2008.01.028

Lee E-B, Hwang I-S, Cha J-H, Lee H-J, Lee W-B, Pak JJ, Lee J-H, Ju B-K (2011) Micromachined catalytic combustible hydrogen gas sensor. Sensors Actuators B Chem 153:392–397. https://doi.org/10.1016/j.snb.2010.11.004

Li Y, Wlodarski W, Galatsis K, Moslih SH, Cole J, Russo S, Rockelmann N (2002) Gas sensing properties of p-type semiconducting Cr-doped TiO_2 thin films. Sensors Actuators B Chem 83:160–163. https://doi.org/10.1016/S0925-4005(01)01031-0

Li C, Zhang D, Liu X, Han S, Tang T, Han J, Zhou C (2003) In_2O_3 nanowires as chemical sensors. Appl Phys Lett 82:1613–1615. https://doi.org/10.1063/1.1559438

Lim C, Wang W, Yang S, Lee K (2011) Development of SAW-based multi-gas sensor for simultaneous detection of CO_2 and NO_2. Sensors Actuators B Chem 154:9–16. https://doi.org/10.1016/j.snb.2010.02.057

Liu J, Wang X, Peng Q, Li Y (2006) Preparation and gas sensing properties of vanadium oxide nanobelts coated with semiconductor oxides. Sensors Actuators B Chem 115:481–487. https://doi.org/10.1016/j.snb.2005.10.012

Lu X, Wu S, Wang L, Su Z (2005) Solid-state amperometric hydrogen sensor based on polymer electrolyte membrane fuel cell. Sensors Actuators B Chem 107:812–817. https://doi.org/10.1016/j.snb.2004.12.022

Lu JG, Chang P, Fan Z (2006) Quasi-one-dimensional metal oxide materials-synthesis, properties and applications. Mater Sci Eng R 52:49–91. https://doi.org/10.1016/j.mser.2006.04.002

Lu G, Ocola LE, Chen J (2009a) Room-temperature gas sensing based on electron transfer between discrete tin oxide nanocrystals and multiwalled carbon nanotubes. Adv Mater 21:1–5. https://doi.org/10.1002/adma.200803536

Lu GH, Ocola LE, Chen JH (2009b) Reduced grapheme oxide for room-temperature gas sensors. Nanotechnology 20:Article ID: 445502. https://doi.org/10.1088/0957-4484/20/44/445502

Ma Y, Wang WL, Liao KJ, Kong CY (2002) Study on sensitivity of nano-grain ZnO gas sensors. J Wide Bandgap Mater 10:112–120. https://doi.org/10.1177/1524511X02043537

Mahmood MR, Soga T, Mamat MH, Khusaimi Z, Nor AM (2013) A review on zinc oxide nanostructures: doping and gas sensing. Adv Mater Res 667:329–332. https://doi.org/10.4028/www.scientific.net/AMR.667.329

Manap H, Muda R, O'Keeffe S, Lewis E (2009) Ammonia sensing and a cross sensitivity evaluation with atmosphere gases using optical fiber sensor. Procedia Chem 1:959–962. https://doi.org/10.1016/j.proche.2009.07.239

Marichy C, Pinna N (2013) Carbon-nanostructures coated/decorated by atomic layer deposition: growth and applications. Coord Chem Rev 257:3232–3253. https://doi.org/10.1016/j.ccr.2013.08.007

Marichy C, Russo PA, Latino M, Tessonnier J-P, Willinger M-G, Donato N, Neri G, Pinna N (2013) Tin dioxide-carbon heterostructures applied to gas sensing: structure-dependent properties and general sensing mechanism. J Phys Chem C 117:19729–19739. https://doi.org/10.1021/jp406191x

Marsal A, Dezanneau G, Cornet A, Morante JR (2003) A new CO_2 gas sensing material. Sensors Actuators 95:266–270. https://doi.org/10.1016/S0925-4005(03)00443-X

Massie C, Stewart G, McGregor G, Gilchrist JR (2006) Design of a portable optical sensor for methane gas detection. Sensors Actuators B Chem 113:830–836. https://doi.org/10.1016/j.snb.2005.03.105

McEntegart CM, Penrose WR, Strathmann S, Stetter JR (2000) Detection and discrimination of coliform bacteria with gas sensor arrays. Sensors Actuators B Chem 70:170–176. https://doi.org/10.1016/S0925-4005(00)00561-X

Mitsubayashi K, Matsunaga H, Nishio G, Ogawa M, Saito H (2004) Biochemical gas sensor (Bio-sniffer) for breath analysis after drinking. In: SICE Annual Conference, Sapporo, Japan, 4–6 August 2004

Morrison RS (1982) Semiconductor gas sensors. Sensors Actuators 2:329–341. ISBN: 978-0-85709-236-6

Neri G (2011) Better sensors through chemistry: some selected examples. Lect Notes Electr Eng 91:19–30. https://doi.org/10.1007/978-94-007-1324-6

Neri G (2015) First fifty years of chemoresistive gas sensors. Chemosensors 3:1–20. https://doi.org/10.3390/chemosensors3010001

Nieuwenhuizen MS, Nederlof AJ (1990) A SAW gas sensor for carbon dioxide and water. Preliminary experiments. Sensors Actuators B Chem 2:97–101. https://doi.org/10.1016/0925-4005(90)80017-T

Ogawa H, Nishikawa M, Abe A (1982) Hall measurement studies and an electrical conduction model of tin oxide ultrafine particle films. J Appl Phys 53:4448–4455. https://doi.org/10.1063/1.331230

Ohsawa I, Ishikawa M, Takahashi K, Watanabe M, Nishimaki K, Yamagata K, Katsura K, Katayama Y, Asoh S, Ohta S (2007) Hydrogen acts as a therapeutic antioxidant by selectively reducing cytotoxic oxygen radicals. Nat Med 13:688–694. https://doi.org/10.1038/nm1577

Okajima H, Kakuma S, Uchida K, Wakimoto Y, Noda K (2006) Measurement of methane gas concentration using infrared LED. In: Proceedings of the international joint conference SICE-ICASE, Busan, 18–21 Oct, pp 1656–1659. https://doi.org/10.1109/SICE.2006.315585

Okazaki S, Nakagawa H, Asakura S, Tomiuchi Y, Tsuji N, Murayama H, Washiya M (2003) Sensing characteristics of an optical fiber sensor for hydrogen leak. Sensors Actuators B Chem 93:142–147. https://doi.org/10.1016/S0925-4005(03)00211-9

Oletic D, Bilas V (2013) Empowering smartphone users with sensor node for air quality measurement. J Phys Conf Ser 450:012028. https://doi.org/10.1088/1742-6596/450/1/012028

Pan ZW, Dai ZR, Wang ZL (2001) Nanobelts of semiconducting oxides. Science 291:1947–1949. https://doi.org/10.1126/science.1058120

Peng S, Cho K (2003) Ab initio study of doped carbon nanotube sensors. Nano Lett 3:513–517. https://doi.org/10.1021/nl034064u

Phawachalotorn C, Sanguanruang O, Ishihara T (2012) Highly selective amperometric sensors for carbon monoxide detection in exhaust gas. Sensors Actuators B Chem 161:635–640. https://doi.org/10.1016/j.snb.2011.10.081

Pijolat C, Pupier C, Sauvan M, Tournier G, Lalauze R (1999) Gas detection for automotive pollution control. Sensors Actuators B Chem 59:195–202. https://doi.org/10.1016/S0925-4005(99)00220-8

Pinna N, Neri G, Antonietti M, Niederberger M (2004) Nonaqueous synthesis of nanocrystalline semiconducting metal oxides for gas sensing. Angew Chem Int Ed 43:4345–4349. https://doi.org/10.1002/anie.200460610

Radhakrishnan R, Virkar AV, Singhal SC, Dunham GC, Marina OA (2005) Design, fabrication and characterization of a miniaturized series-connected potentiometric oxygen sensor. Sensors Actuators B 105:312–321. https://doi.org/10.1016/j.snb.2004.06.014

Ramamoorthy R, Dutta PK, Akbar SA (2003) Oxygen sensors: materials, methods, designs and applications. J Mater Sci 38:4271–4282. https://doi.org/10.1023/A:1026370729205

Righettoni M, Amann A, Pratsinis SE (2015) Breath analysis by nanostructured metal oxides as chemo-resistive gas sensors. Mater Today 18:163–171. https://doi.org/10.1016/j.mattod.2014.08.017

Rothschild A, Komem Y (2004a) The effect of grain size on the sensitivity of nanocrystalline metal-oxide gas sensors. J Appl Phys 95:6374–6380. https://doi.org/10.1063/1.1728314

Rothschild A, Komem Y (2004b) On the relationship between the grain size and gas-sensitivity of chemo-resistive metal-oxide gas sensors with nanosized grains metal oxide gas sensors with nanosized grains. J Electroceram 13:697–701. https://doi.org/10.1007/s10832-004-5178-8

Sadek AZ, Choopun S, Wlodarski W, Ippolito SJ, Kalantar-Zaden K (2007) Characterization of ZnO nanobelt-based gas sensor for H_2, NO_2 and hydrocarbon sensing. IEEE Sensors J 7:919–924. https://doi.org/10.1109/JSEN.2007.895963

Sathiyamoorthi R, Chandrasekaran R, Mathanmohan T, Muralidharan B, Vasudevan T (2004) Study of electrochemical based gas sensors for fluorine and chlorine. Sensors Actuators B Chem 99:336–339. https://doi.org/10.1016/j.snb.2003.11.031

Seiyama T (1988) Chemical sensors-current status and future outlook. In: Seiyama T (ed) Chemical sensor technology. Elsevier, Amsterdam

Seiyama T, Kato A (1962) A new detector for gaseous components using semiconductor thin film. Anal Chem 34:1502–1503. https://doi.org/10.1021/ac60191a001

Sharma S, Madou M (2012) A new approach to gas sensing with nanotechnology. Phil Trans R Soc A 370:2448–2473. https://doi.org/10.1098/rsta.2011.0506

Shaver PJ (1967) Activated tungsten oxide gas detectors. Appl Phys Lett 11:255–257. https://doi.org/10.1063/1.1755123

Shaw G, Parkin IP, Pratt KFE, Williams DE (2005) Control of semiconducting oxide gas-sensor microstructure by application of an electric field during aerosol-assisted chemical vapor deposition. J Mater Chem 15:149–154. https://doi.org/10.1039/b411680a

Shimanoe K, Yuasa M, Kida T, N. Yamazoe (2011) Semiconductor gas sensor using nano-sized oxide for high-sensitive detection of environment-related gases. In: Proceedings of the IEEE international conference on nanotechnology materials and devices, October, pp 38–43. https://doi.org/10.1109/NMDC.2011.6155309

Shimizu Y, Egashira M (1999) Basic aspects and challenges of semiconductor gas sensors. MRS Bull 24:18–24. https://doi.org/10.1557/S0883769400052465

Shin W, Matsumiya M, Izu N, Murayama N (2003) Hydrogen-selective thermoelectric gas sensor. Sensors Actuators B Chem 93:304–308. https://doi.org/10.1016/S0925-4005(03)00225-9

Shin W, Matsumiya M, Qiu F, Izu N, Murayama N (2004) Thermoelectric gas sensor for detection of high hydrogen concentration. Sensors Actuators B Chem 97:344–347. https://doi.org/10.1016/j.snb.2003.08.029

Shin W, Nishibori M, Izu N, Itoh T, Matsubara I, Nose K, Shimouchi A (2011) Monitoring breath hydrogen using thermoelectric sensor. Sens Lett 9:684–687. https://doi.org/10.1166/sl.2011.1591

Shin W, Itoh T, Izu N (2015) Health care application of gas sensors. Synthesiol Engl Ed 8:211–219. https://doi.org/10.5571/syntheng.8.4_211

Simon I, Arndt M (2002) Thermal and gas-sensing properties of a micromachined thermal conductivity sensor for the detection of hydrogen in automotive applications. Sensors Actuators A 97–98:104–108. https://doi.org/10.1016/S0924-4247(01)00825-1

Sin MLY, Chow GCT, Wong GMK, Li WJ, Leong PHW, Wong KW (2007) Ultralow-power alcohol vapor sensors using chemically functionalized multiwalled carbon nanotubes. IEEE Trans Nanotechnol 6:571–577. https://doi.org/10.1109/TNANO.2007.900511

Suehiro J, Zhou G, Hara M (2003) Fabrication of a carbon nanotube based gas sensor using dielectrophoresis and its application for ammonia detection be impedance spectroscopy. J Phys D Appl Phys 36:109–114. https://doi.org/10.1088/0022-3727/36/21/L01

Sun YP, Fu KF, Lin Y, Huang WJ (2002) Functionalized carbon nanotubes: properties and applications. Acc Chem Res 35:1096–1104. https://doi.org/10.1021/ar010160v

Sun Y-F, Liu S-B, Meng F-L, Liu J-Y, Jin Z, Kong L-T, Liu J-H (2012) Metal oxide nanostructures and their gas sensing properties: a review. Sensors 12:2610–2631. https://doi.org/10.3390/s120302610

Taguchi N (1971) Gas detecting devices. U.S. Patent 3,631,436

Takada T, Fukunaga T, Maekawa T (2000) New method for gas identification using a single semiconductor sensor. Sensors Actuators B Chem 66:22–24. https://doi.org/10.1016/S0925-4005(98)00254-8

Tardy P, Coulon J-R, Lucat C, Menil F (2004) Dynamic thermal conductivity sensor for gas detection. Sensors Actuators B Chem 98:63–68. https://doi.org/10.1016/j.snb.2003.09.019

Tricoli A, Pratsinis SE (2010) Dispersed nanoelectrode devices. Nat Nanotechnol 5:54–60. https://doi.org/10.1038/nnano.2009.349

Tricoli A, Righettoni M, Pratsinis SE (2009) Minimal cross-sensitivity to humidity during ethanol detection by SnO_2-TiO_2 solid solutions. Nanotechnology 20:315502. https://doi.org/10.1088/0957-4484/20/31/315502

Tricoli A, Righettoni M, Teleki A (2010) Semiconductor gas sensors: dry synthesis and application. Angew Chem Int Ed 49:7632–7659. https://doi.org/10.1002/anie.200903801

Venema A, Nieuwkoop E, Ghijsen WJ, Barendsz AW, Nieuwenhuizen MS (1987) NO_2 Gas-concentration measurement with a SAW chemosensor. IEEE Trans Ultrason Ferroelectr Freq Control 34:148–155. https://doi.org/10.1987/ITUFF.34.148V

Viricelle JP, Pijilat C, Riviere B, Rotureau D, Briand D, DeRooij NF (2006) Compatibility of screen printing technology with microhotplate for gas sensor and solid oxide micro fuel cell development. Sensors Actuators B Chem 118:263–268. https://doi.org/10.1016/j.snb.2006.04.031

Wang X, Carey WP, Yee SS (1995) Monolithic thin film metal oxide gas sensor arrays with application to monitoring of organic vapors. Sensors Actuators B Chem 28:63–70. https://doi.org/10.1016/0925-4005(94)01531-L

Wang W, Huang H, Li Z, Zhang H, Wang Y, Zheng W, Wang C (2008) Zinc oxide nanofiber gas sensors via electrospinning. J Am Ceram Soc 91:3817–3819. https://doi.org/10.1111/j.I551-2916.2008.02765.x

Wang C, Yin L, Zhang L, Xiang D, Gao R (2010) Metal oxide gas sensors: sensitivity and influencing factors. Sensors 10:2088–2016. https://doi.org/10.3390/s100302088

Wei B-Y, Hsu M-C, Su P-G, Lin H-M, Wu R-J, Lai H-J (2004) A novel SnO_2 gas sensor doped with carbon nanotubes operating at room temperature. Sensors Actuators B Chem 101:81–89. https://doi.org/10.1016/j.snb.2004.02.028

Willinger MG, Neri G, Rauwel E, Bonavita A, Micali G, Pinna N (2008) Vanadium oxide sensing layer grown on carbon nanotubes by a new atomic layer deposition process. Nano Lett 8:4201–4204. https://doi.org/10.1021/nl801785b

Wilson AD, Baietto M (2009) Applications and advances in electronic-nose technologies. Sensors 9:5099–5148. https://doi.org/10.3390/s90705099

Wohltjen H, Dessy R (1979) Surface acoustic wave probe for chemical analysis. II. Gas chromatography detector. Anal Chem 51:1458–1478. https://doi.org/10.1021/ac50045a025

Wolkenstein FF (1961) Effect of ionizing radiation on the adsorptive and catalytic properties of semiconductors. Discuss Faraday Soc 31:209–218. https://doi.org/10.1039/DF9613100209

Xu C, Jun Tamaki J, Miura N, Yamazoe N (1991) Grain size effects on gas sensitivity of porous SnO_2-based elements. Sensors Actuators B Chem 3:147–155. https://doi.org/10.1002/anie.200903801

Xu L, Li T, Gao X, Wang, Y, Zheng R, Xie L Lee L (2010) Behavior of a catalytic combustion methane gas sensor working on pulse mode. In: Proceedings of the IEEE international conference on sensors, Kona, HI, USA, 1–4, 391–394. https://doi.org/10.1109/ICSENS.2010.5690213

Yamazoe N (1991) New approaches for improving semiconductor gas sensors. Sensors Actuators B Chem 5:7–19. https://doi.org/10.1016/0925-4005(91)80213-4

Yamazoe N (2005) Toward innovations of gas sensor technology. Sensors Actuators B Chem 108:2–14. https://doi.org/10.1016/j.snb.2004.12.075

Yamazoe N, Miura N (1994) Environmental gas sensors. Sensors Actuators B Chem 20:95–102. https://doi.org/10.1016/0925-4005(93)01183-5

Yamazoe N, Shimanoe K (2008) Theory of power laws for semiconductor gas sensors. Sensors Actuators B Chem 128:566–573. https://doi.org/10.1016/j.snb.2007.07.036

Yamazoe N, Shimanoe K (2009) Receptor function and response of semiconductor gas sensor. J Sens 2009:875704. https://doi.org/10.1155/2009/875704

Yamazoe N, Kurokawa Y, Seiyama T (1983) Effects of additives on semiconductor gas sensors. Sensors Actuators B Chem 4:283–289. https://doi.org/10.1016/0250-6874(83)85034-3

Yan Y, Miura N, Yamazoe N (1995) Potentiometric sensor using stabilized zirconia for chlorine gas. Sensors Actuators B Chem 24:287–290. https://doi.org/10.1016/0925-4005(95)85062-7

Yang J-C, Dutta PK (2010) High temperature potentiometric NO_2 sensor with asymmetric sensing and reference Pt electrodes. Sensors Actuators B Chem 143:459–463. https://doi.org/10.1016/j.snb.2009.09.023

Yeom J, Oh I, Field C, Radadia A, Ni Z, Bae B, Han J, Masel RI, Shannon MA (2008) Enhanced toxic gas detection using a MEMS pre-concentrator coated with metal organic framework absorber. In: Proceedings of MEMS, Tucson, AZ, 13–17 January 2008. https://doi.org/10.1109/MEMSYS.2008.4443635

Yoon S, Lee C, Kim Y (2009) A thermoelectric gas sensor based on an embedded tin oxide catalyst for detecting hydrogen and NO_x gases. In: Proceedings of the IEEE 22nd international conference on micro electro mechanical systems (MEMS '09), Sorrento, pp 272–275. https://doi.org/10.1109/MEMSYS.2009.4805371

Yunusa Z, Hamidon MN, Kaiser A, Awang Z (2014) Gas sensors: a review. Sens Transducers 168:61–75

Zemel J (1988) Theoretical description of gas–film interaction on SnO_x. Thin Solid Films 163:189–202. https://doi.org/10.1016/0040-6090(88)90424-5

Zhang T, Mubeen S, Myung VN, Deshusses MA (2008) Recent progress in carbon nanotube-based gas sensors. Nanotechnology 19:Article ID: 332001. https://doi.org/10.1088/0957-4484/19/33/332001

Zhang G, Li Y, Li QA (2010) Miniaturized carbon dioxide gas sensor based on infrared absorption. Opt Lasers Eng 48:1206–1212. https://doi.org/10.1016/j.optlaseng.2010.06.012

Zhu L, Zeng W (2017) Room-temperature gas sensing of ZnO-based gas sensor: a review. Sensors Actuators A 267:242–261. https://doi.org/10.1016/j.sna.2017.10.021

Index

A
Abbas, S., 209
Abd-elsalam, K.A., 254
Abdrakhimov, R.R., 106
Abou-Gamra, Z.M., 16
Accumulation, 6, 50, 51, 53, 59, 60, 66, 69, 73, 75, 106, 185, 244, 250, 262, 280, 287–290, 295, 298, 299
Acquaroli, L.N., 318
Activated carbon (AC), 7–11, 19, 21, 125, 126, 132, 135, 146, 147, 152
Adsorption technology, 6–22
Agboola, O., 2–34
Agrawal, S., 250
Agriculture, 144, 244–248, 252, 256, 259, 261, 263, 264, 266, 267, 269, 278, 296, 297, 299, 307
Ahmed, K., 210
Ahmad, R., 144–162
Ahmed, M.A., 16
Anarjan, N., 211
Arunkumar, R., 217
Alappat, B.J., 118–136
Alemdar, A., 269
Ali, Z., 144–162
Alimakan, E., 119
Alireza, S., 120
Ambasta, R.C., 64
Andronic, L., 16
Anisimkin, V.I., 322
Anjali, C.H., 268
Anuradha, S., 313
Arndt, M., 313
Arora, R., 248
Arya, A., 119
Ashraf, S., 338
Azadbakht, P., 185
Aziz, C.T., 30

B
Babu, S., 119
Bacteria, 13, 14, 23–25, 31, 148, 149, 152, 155, 156, 159, 184, 185, 252–255, 263, 264, 284, 290, 297
Bahmani, S.H., 120
Bahmani, Z., 166–193
Bardeen, J., 308
Barsan, N., 330
Bazhenov, V., 112
Beck, K., 322
Ben-Moshe, T., 128
Berlin, J.M., 65
β-carotene, 207, 208, 214–216, 218, 219, 223–226, 228–230, 233, 234
Bhatnagar, A., 185
Biological denitrification, 168, 184, 185, 194
Bio-remediation, 5
Blokhin, A.N., 101, 105
Bowen, P., 263
Bradford, S.A., 125
Brattain, W.H., 308
Brunauer, S., 52
Byrne, J.A., 268

C
Canas, J.E., 249
Cancers, 33, 49, 59–62, 74–76, 204, 343
Capacitive deionization (CDI), 168, 190–191, 195

N. Dasgupta et al. (eds.), *Environmental Nanotechnology Volume 3*, Environmental Chemistry for a Sustainable World 27, https://doi.org/10.1007/978-3-030-26672-1

Carbon nanotubes (CNT), 8, 92, 119, 146, 245, 288, 314
Carotenoids, 204–235, 267
Carstens, J.F., 124, 126
Cavity, 60, 321
Chandrasekaran, N., 268
Chaniotakis, N.A., 268
Chao, Y., 316
Chen, D., 318
Chen, H., 255, 318
Chen, K., 248
Chen, P., 166–193
Chitosan, 14, 15, 22, 147, 149, 150, 217, 260
Cho, B., 334
Choi, Y.J., 337
Choobbasti, A.J., 120
Chowdhury, I., 125
Chrysikopoulos, C.V., 125, 126, 134
Composites, 8, 21, 23–27, 30, 31, 91–112, 145, 176, 177, 181–183, 193, 246, 250, 254, 327
Conducting polymers, 316, 326
Creixell, M., 65
Cukrov, L.M., 336
Currie, J.F., 314

D
Darnault, C.J.G., 125
Davidov-Pardo, G., 211
de Freitas Zômpero, R.H., 213
de Graaf, G., 313
De la Rosa, G., 248
Denitrification processes, 166–193
DeRosa, M.C., 261
Dessy, R., 321
Disinfections, 24, 32, 33, 147–149, 151–153, 162, 254, 255, 264
Domingos, R.F., 125, 127
Doshi, R., 125
Dunlop, P.S.M., 268
Duta, A., 16
Dutta, A., 316

E
Economy, J., 264
EL Badawi, N.A.A.H., 30
Elimelech, M., 130, 133
Elkady, M.F., 307–346
El-Sayed, I.H., 65
El-Temsah, Y.S., 249
Emmett, P.H., 52
Ensor, D.S., 31
Environmental monitoring, 309, 340, 341
Environments, 3, 50, 107, 118, 144, 167, 214, 244, 279, 307
Esawi, 30

F
Factors, 7, 8, 11, 15, 18, 21, 27, 64–67, 71, 74, 75, 93, 94, 96, 100, 101, 111, 122, 126–136, 166, 169, 180, 183, 185, 186, 189, 205, 208, 215, 221, 227, 230–233, 235, 264, 266, 267, 279–287, 291, 294–299, 325, 326, 331, 343
Fang, J., 125
Fate, 13, 33, 50, 122, 124–136, 161, 162, 225, 279–281, 283, 285, 287, 291, 297–299
Fatoba, O.S., 2–34
Fayomi, S.O., 2–34
Feng, B.H., 260
Fernandez-Perez, M., 260
Fillers, 23, 25, 93–96, 100, 101, 103, 106, 111, 112, 225
Fischerauer, G., 322
Flores-Cespedes, F., 260
Foods, 149, 161, 162, 204–235, 244, 245, 252, 253, 256, 257, 261, 265–269, 278–281, 289, 294, 296, 299, 307, 344, 346
Frandsen, M.V., 260
French, R.A., 125
Fujishima, A., 178
Fullerenes, 9, 59, 92, 152, 153, 160, 246, 248, 268, 279, 295

G
Gabaldón, C., 125
Gan, T., 314
Garcia-R.D., 318
Garg, D., 244–269
Gas sensors, 267, 307–346
Gas sensors applications, 307–346
Ghaee, A., 189
Ghormade, V., 265
Ghosh, A.K., 264
Girgis, E.A., 30
Girschikofsky, M., 318
Godinez, I.G., 125
Goldshtein, R., 260
Gong, Y., 121
Gopel, W., 328

Gottschalk, F., 123
Groundwater treatment, 188
Gurlo, A., 331

H
Halas, N.J., 71
Halek, G., 324
Hamid, S., 178
Han, B., 121
Hassan, H.S., 307–346
Ha, T.V.A., 211
Häyrynen, K., 190
He, F., 121, 122, 125
Heiland, G., 308
Hellmann, C., 260
Ho, K.-C., 316
Ho, Y.S., 127
Hoek, E.M.V., 264
Honda, K., 178
Horii, A., 248
Hu, R., 314
Huang, J., 323
Hung, W.-T., 316
Hussain, S., 248
Hwang, I.C., 260
Hwang, Y.H., 170, 171
Hyperthermia, 51, 62, 66, 70–72, 76

I
Ibrahim, E.A, 248
Inorganic nanomaterials, 49, 156, 246, 247
Interactions, 7, 9–11, 18, 19, 21, 51, 53, 57, 59, 60, 63, 65–67, 71, 74, 97, 98, 118–136, 146, 152, 153, 180, 185, 188, 204, 205, 208, 215, 217, 223–226, 229–232, 234, 254, 261, 266, 267, 278–299, 307, 326–328
Inyang, M., 125
Ionic strengths (IS), 10, 55, 127–129, 131, 133, 135, 136, 157, 206, 215, 217, 230, 283–286, 291, 297
Isiklan, N., 260
Ivitskiy, I., 111

J
Jain, A., 119
Jaisi, D.P., 130
Jakubik, W.P., 322
Jana, T., 260
Jarunglumlert, T., 226
Jiana, M., 19
Jiang, X., 128
Johnson, R.P., 130
Joner, E.J., 249
Jones, E.H., 125
Joseph, S., 119

K
Karn, B., 119
Kas, O.Y., 31
Kasai, N., 319
Kasel, D., 125
Khalid, N., 120
Kheiri, T., 261
Khodadadi, A., 323
Khodakovskaya, M., 247
Khodakovskaya, M.V., 249, 255
Kim, D., 211
King, W.H., 319
Kok, F.N., 260
Kolosov, A.E., 91–112
Kolosova, E.P., 91–112
Komem, Y., 333
Kopec, R.E., 228
Korotcenkov, G., 323, 334, 340
Kulkarni, A.R., 260
Kumar, A., 118–136, 278–299
Kuroda, S., 65

L
Lado, J.J., 191
Lahiani, M.H., 255
Larue, C., 249
Lee, C., 317
Lee, E.-B., 312
Lee, H., 322
Lee, S.W., 331, 332
Lee, W.M., 249
Lee, Y.C., 335
Li, J., 75
Li, M., 260
Li, Z., 75
Lin, D., 247, 249
Lin, K.C., 125
Lin, S., 293
Lin, V.S.-Y., 251, 268
Liou, Y.H., 175
Liu, H., 177
Liu, H.B., 171

Liu, H.F., 121
Liu, J., 335
Liu, Q., 251
Liu, R., 121
Liu, T., 14
Liu, Y., 260
Loha, K.M., 260
Lohith Kumar, D.H., 204–235
Lopez-Moreno, M.L., 249
Lu, C., 247, 249
Lu, G., 314
Lu, G.H., 314
Lu, X., 316
Luo, T., 16
Lupu, A.-R., 49

M
Ma, Y., 333
Mahakham, W., 248
Majeed, S., 24
Manap, H., 318
Martin-Ortigosa, S., 251
Massie, C., 318
McAleer, 312
McKay, G., 127
McMurray, T.A., 268
Melancon, M.P., 65
Membranes, 9, 60, 145, 177, 206, 250, 292, 314
Membrane technologies, 23, 156, 186–190, 192
Metal oxide semiconductors (MOSs), 323, 324, 328–338, 341, 344, 345
Milani, N., 268
Miralles, P., 249
Mirbagheri, N.S., 166–193
Mirzajani, F., 249
Mitra, J., 204–235
Mixtures, 21, 27, 30, 99, 100, 105, 119, 122, 133–136, 172, 191, 207, 221, 223, 225, 285, 288, 289, 294–297, 299, 308, 310, 313, 337, 339, 341, 342
Moaveni, P., 261
Modifications, 17, 18, 21, 23, 25, 28, 49, 51, 57, 58, 91–112, 129–131, 133, 155, 181, 188, 189, 191, 204, 223, 268, 325
Mohsenzadeh, M., 195
Mondal, A., 249
Moraes, M., 213
Morla, S., 249
Morrison, R.S., 328
Mueller, N.C., 123
Mukherjee, A., 268
Mun, S., 218

N
Nair, R., 246, 248
Nangmenyi, G., 264
Nano-additives, 119
Nano-adsorption, 6–22
Nanoencapsulation, 204–235, 278
Nanofibers, 27–29, 31, 155, 268
Nanomaterials, 3–5, 7, 9, 17, 18, 23, 27, 32–34, 49, 98, 118–136, 144–146, 149, 153, 156, 158, 161, 162, 166–193, 244–269, 278–281, 294, 295, 307–346
Nanomembranes, 23–29, 262, 335
Nanoparticles (NPs), 3, 92, 118, 147, 168, 216, 245, 278, 307
Nanosensors, 265, 266, 268, 269, 278, 314
Nano-silver, 156, 253
Nanotechnologies, 3, 91, 123, 144, 193, 205, 245, 278, 307
Nanotubes, 9, 59, 92, 125, 146, 246, 279, 327
Nano zero valent iron (NZVI), 14, 31, 168–176
Natural organic matter (NOM), 15, 25, 26, 126, 128, 129, 133, 136
Nieuwenhuizen, M.S., 322
Nima, 251
Nitrate contamination, 167, 169
Nohani, E., 119
Nowack, B., 123

O
Ogawa, H., 331
Ohsawa, I., 342
Okajima, H., 318
Okazaki, S., 318
Oligomers, 91–112
Ortashi, K.M.O., 30
Osteryoung, 317

P
Pan, G., 121
Park, C., 65
Park, S.-C., 312
Parsai, T., 118–136
Patents, 3, 29–32, 192–193, 259
Pavlova-Verevkina, O.B., 125
Payasi, D.K., 244–269
Pelaez, M., 255
Pelley, A.J., 132
Peng, L.F., 260
Peptides, 66, 98, 147, 252

Pettibone, J.M., 125, 127
Photocatalytic denitrification, 178–183, 194
Photodynamic therapy (PDT), 62, 69, 72–74, 76
Pinna, N., 335
Piplai, T., 118–136
Plants, 26, 118, 148, 166, 228, 245, 278
Plasmonic photothermal therapy (PPTT), 71, 72
Popescu, T., 49
Popoola, P., 2–34
Porous medium, 124, 126–128, 130, 131, 134, 136
Prasad, T.N.V.K.V., 249
Productions, 14, 24, 25, 29, 31, 32, 62, 65, 73, 92–96, 112, 124, 148, 151–153, 157, 158, 166, 168, 169, 171, 176, 179, 190, 194, 216, 220, 228, 245, 247–267, 269, 280, 299, 308, 344
Properties, 3, 92, 122, 145, 168, 245, 278, 307

Q
Qian, C., 209
Qian, Y., 65
Quaglia, F., 260
Qv, X.-Y., 217

R
Radhakrishnan, R., 317
Ragaei, M., 260
Rajakumar, G., 255
Raliya, R., 249
Ramadan, 30
Rathore, P., 250
Reactoplasts, 92, 93, 96, 97, 100, 101, 108, 109, 112
Rico, C.M., 250
Riedel, R., 331
Rocha-Selmi, G.A., 217
Roopa, S.S., 204–235
Roots, 167, 247–250, 259, 263, 266, 278–299
Rothschild, A., 333
Rozhkova, E.A., 73

S
Sabbaghi, S., 166–193
Sabry, A.-K.H., 260
Sadek, A.Z., 335, 336
Sadiku, R., 2–34
Saien, J., 30
Sain, M., 269
Sáiz-Abajo, M.-J., 215
Shafaa, M.W.I., 212
Silva, D.F., 217
Sotomayor-Gerding, D., 211, 234
Sanni, E.S., 2–34
Sari, T., 210
Sathiyamoorthi, R., 314
Sberveglieri, G., 328
Schneider, C.S., 59
Schrick, B., 131
Seetha, N., 126, 134
Seiyama, T., 308, 309, 323
Sensing materials, 308, 309, 320, 324–338, 340, 344
Sensitivity, 9, 67, 218, 252, 308, 311, 313, 314, 317, 318, 320, 322–326, 329, 331–335, 338, 340–342, 344, 345
Shani, C., 125
Sharma, Y., 268
Shaver, P.J., 308
Shaw, G., 338
Shestakov, P.D., 110
Shimanoe, K., 324
Shin, W., 312
Siddiqui, M.H., 247
Silva, D.F., 251
Simon, I., 313
Singh, D., 278–299
Singh, S., 252
Sivetskyy, V.I., 112
Smart delivery systems, 244, 265, 278
Soils, 6, 118, 152, 167, 244, 279
Solovitch, N., 125
Stampoulis, D., 249
Stojanović, M., 49
Su, C., 125
Surface chemistry, 7, 8, 11, 28, 132, 133, 344
Suriyaprabha, R., 247, 249
Syngouna, V.I., 125, 126, 134

T
Tacke, T., 177
Taguchi, N., 308, 323
Taha, M.R., 120
Taha, O.M., 120
Takada, T., 324
Tan, C., 212, 213
Tang, C., 176
Tarafdar, J.C., 249
Tardy, P., 313
Targeted therapies, 63, 67, 75
Teller, E., 52

Titania, 148, 149, 156, 158–160, 162, 325, 342
Torkzaban, S., 125
Torney, F., 251, 268
Transport, 6, 23, 24, 95, 121, 122, 124–136, 175, 191, 206, 214, 216, 224, 228, 232, 279, 280, 284, 285, 287, 291–294, 297, 299, 328, 329, 335
Trewyn, B.G., 268
Tricoli, A., 331, 334
Tseng, W.J., 125
Tufenkji, N., 132
Tungittiplakorn, W., 121

U
Ultrasonics, 91–112
Upadhyaya, H., 247
Uptake, 18, 53, 60, 61, 67, 68, 73, 145, 215, 227–229, 232–234, 247, 248, 253, 259, 261, 262, 278–299

V
Vamvakaki, V., 268
Venema, A., 322
Viruses, 31, 125, 126, 134, 152, 153, 155, 159, 246, 252, 255, 264, 265
Visa, M., 16
Vishwanathan, R., 210
Vorlop, 177

W
Walshe, G.E., 126
Wan Yaacob, W.Z., 121
Wan, Q., 323
Wang, C., 131
Wang, K., 251, 268
Wang, X., 249
Wang, Y., 65
Wastewater treatment, 3, 4, 7, 24, 25, 28, 30–34, 245, 288
Water treatment, 5–23, 26, 32, 33, 144–162, 193
Waznea, M., 125
Weimar, U., 330
Wohltjen, H., 321
Wolffenbuttel, R., 313
Wolkenstein, F.F., 328
Wright, J.E., 260
Wu, S.G., 249

X
Xia, S., 212
Xia, Z., 212
Xie, J., 73
Xing, B., 247, 249
Xiong, Z., 122
Xu, C., 333, 334
Xu, D., 208
Xu, L., 311
Xu, Y., 121

Y
Yamazoe, N., 328, 329
Yan, Y., 317
Yang, F., 249
Yang, F.L., 260
Yang, J.-C., 317
Yang, L., 249
Yang, P.D., 328
Yang, Y., 24
Yao, K.S., 252
Yea, B., 324
Yeom, J., 335
Yin, J., 24
Yokoyama, T., 65
Yoon, S., 312
Yuan, C., 224
Yuan, Y., 209

Z
Zhang, G., 119, 319
Zhang, T., 314
Zhang, X.Q., 65
Zhang, Z., 218
Zhao, D., 121
Zhao, L., 292
Zhao, L.J., 130
Zheng, L., 247
Zinc oxides (ZnO), 8, 59, 123, 124, 130, 133–135, 148, 149, 189, 246–249, 254, 268, 279, 285, 287, 288, 295, 308, 324, 325, 334, 335
Zodrow, K., 25