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Nanoscience in Food and Agriculture 3

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Sustainable agriculture is a rapidly growing field aiming at producing food and energy in a sustainable way for humans and their children. Sustainable agriculture is a discipline that addresses current issues such as climate change, increasing food and fuel prices, poor-nation starvation, rich-nation obesity, water pollution, soil erosion, fertility loss, pest control, and biodiversity depletion.

Novel, environmentally-friendly solutions are proposed based on integrated knowledge from sciences as diverse as agronomy, soil science, molecular biology, chemistry, toxicology, ecology, economy, and social sciences. Indeed, sustainable agriculture decipher mechanisms of processes that occur from the molecular level to the farming system to the global level at time scales ranging from seconds to centuries. For that, scientists use the system approach that involves studying components and interactions of a whole system to address scientific, economic and social issues. In that respect, sustainable agriculture is not a classical, narrow science. Instead of solving problems using the classical painkiller approach that treats only negative impacts, sustainable agriculture treats problem sources.

Because most actual society issues are now intertwined, global, and fast-developing, sustainable agriculture will bring solutions to build a safer world. This book series gathers review articles that analyze current agricultural issues and knowledge, then propose alternative solutions. It will therefore help all scientists, decision-makers, professors, farmers and politicians who wish to build a safe agriculture, energy and food system for future generations.

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Nanoscience in Food and Agriculture 3

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We dedicate this book to our parents
– The Editors

Nano-foods: arriving at stores near you
– Shivendu Ranjan and Nandita Dasgupta

Preface

Nanomaterials with unique properties are now being used to improve food and agricultural production. Research on nanomaterials is indeed revealing new applications that were once thought to be imaginary. Specifically, applications lead to higher crop productivity with nanofertilizers, better packaging, longer food shelf life, and better sensing of aromas and contaminants. These applications are needed in particular in poor countries where food is scarce and the water quality bad. Nanotechnology also addresses the age-old issue of water polluted by industrial,

Fig. 1 Nanotechnology for improving quality of water and food. Left: the Roanne river, Saillans area, Vercors, French Alps. Copyright: Alain Beguey/INRA. Right: a malnourished girl of a developing country – Tamil Nadu, India. Copyright: Kamal Dasgupta/Sarojini Nagar/Lucknow/India

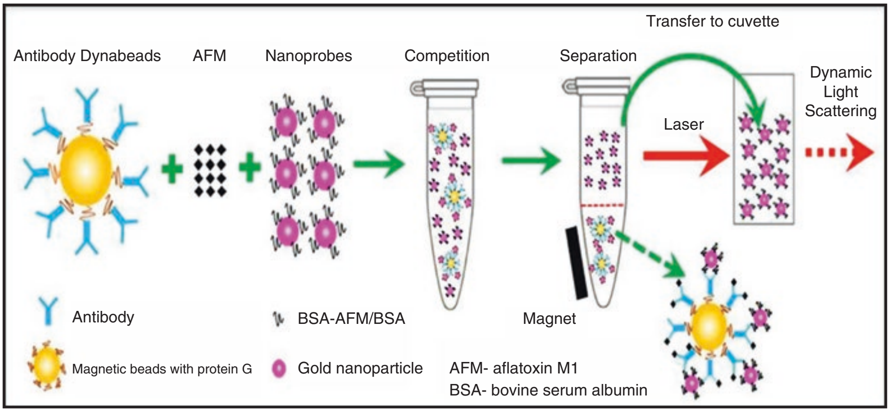

Fig. 2 Dynamic light scattering detection of aflatoxin M1 using gold nanoparticle-based probes. Kumar et al., Chap. 6

urban, and agricultural pollutants. For instance, research produces nanomaterials that clean water more efficiently than classical methods, thus yielding water for drinking and irrigation. However, some nanomaterials have been found to be toxic. Therefore, nanomaterials should be engineered to be safe for the environment. In this book we present ten chapters describing the synthesis and application of nanomaterials for health, food, agriculture, and bioremediation. This book is the third volume on *Nanoscience in Food and Agriculture*, published in the series *Sustainable Agriculture Reviews* (http://www.springer.com/series/8380).

Detailed classifications of nanomaterials are provided by Mageswari et al. in Chap. 2 and by Madhumitha et al. in Chap. 4. The use of copper nanoparticles in agriculture is discussed by Shahmoradi and Byrappa in Chap. 1 and by Kasana et al. in Chap. 5. The transition from nutraceuticals to nanoceuticals is summarized by Kakkar et al. in Chap. 7. Kumar et al. review the applications of nanomaterials to detect food contaminants in Chap. 6 (Fig. 2).

Removal of nitrate, phosphate, and agricultural toxins from water using nanoscale materials is discussed in Chap. 8 by Prashantha Kumar and in Chap. 9 by Leong et al. Pandiarajan et al. discuss the toxicity mechanism of commonly used silver nanoparticles in Chap. 3. Pramanik and Pramanik review the future of nanotechnology for sustainable agriculture in India in Chap. 10.

Thanks for reading.

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Contents

About the Editors

Shivendu Ranjan is currently working as DBT Research Fellow, Department of Biotechnology, Ministry of Science and Technology, Govt. of India, at VIT University, Vellore, Tamil Nadu, India. He is also serving for a nongovernment organization as an honorary director, Research Wing, Veer Kunwar Singh Memorial Trust, Chapra, Bihar, India. He is the founder director at Xpert Arena Technological Services Pvt. Ltd., India (www.xpertarena.com); this company is dedicated to serve in online and offline sectors with a vision to simplify education. He has also founded and drafted the concept for the first edition of *VIT Bio Summit* in 2012, and the same has been continued till date by the university.

His area of research is multidisciplinary which is but not limited to nano-food technology, nano-agri-technology, nanobiotechnology, nano-toxicology, natural products technology, natural products chemistry, bio-business, food chemistry, and food engineering. He has published many scientific articles in international peer-reviewed journals and is also serving as editorial board member and referee for reputed international peer-reviewed journals. He has bagged several awards from different organizations, e.g., best poster award, achiever award, research award, young researcher award, etc.

Nandita Dasgupta is currently serving as research associate at VIT University, Vellore, Tamil Nadu, India. She has exposure to research institutes and industries including CSIR (Central Food Technological Research Institute), Mysore, India, and Uttar Pradesh Drugs and Pharmaceutical Co. Ltd., Lucknow, India. Her areas of interest include toxicological analysis, natural products technology, nanobiotechnology, and agri-food technology.

She has published many scientific articles in international peer-reviewed journals and is also serving as editorial board member and referee for reputed international peer-reviewed journals. She has received the certificate for "Outstanding Contribution" in Reviewing from Elsevier, the Netherlands. She has also been nominated for advisory panel for Elsevier, the Netherlands. She was the guest editor in the *Journal of Chemistry* for the special issue entitled "Food Nanotechnology Opportunities and Challenges." She has received several awards from different organizations, e.g., best poster award, young researcher award, special achiever award, research award, etc.

Eric Lichtfouse, 56, is a soil scientist at the French National Institute for Agricultural Research (INRA). He has invented the ^{13}C-dating method[1] allowing to measure the dynamics of soil organic molecules, thus opening the field of molecular-level investigations of soil carbon sequestration. Chief editor of the awarded journal *Agronomy for Sustainable Development*[3], he has raised the journal rank from 29/53 in 2003, with an impact factor of 0.56, to 2/81 in 2014, with an impact factor of 3.99, in the agronomy category. He is also chief editor and founder of the journal *Environmental Chemistry Letters*[4] and the book series *Sustainable Agriculture Reviews*[5]. He is lecturing scientific writing and communication in universities worldwide[6]. His publication assistance service at the INRA has founded the French-English newsletter Publier La Science[7]. He has published the book

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[1] http://dx.doi.org/10.1007/s10311-011-0334-2

[2] http://archive.sciencewatch.com/inter/jou/2010/10novAgrSusDev

[3] http://www.springer.com/journal/13593

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[7] https://www.youtube.com/playlist?list=PLKEz5Pbi4p3By53Q0gclKPeSBTK2HJGK_

Scientific Writing for Impact Factor Journal[8]. This textbook describes in particular the micro-article[9], a new tool to identify the novelty of experimental results. Further details are available on SlideShare[10], LinkedIn[11], ResearchGate[12], ResearcherID[13], and ORCID[14].

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Chapter 1
Fabrication, Characterization and Applications of Metal Oxide-Doped ZnO Hybrid Nanomaterials

Behzad Shahmoradi and K. Byrappa

Abstract Zinc oxide (ZnO) is a versatile material having various applications in different disciplines. ZnO is an excellent alternative for TiO_2 for the photodegradation of environmental pollutants. However, pure ZnO has some drawbacks, which limits photodegradation applications. ZnO photocatalytic activity is limited to the UV region. Moreover, ZnO gets agglomerated in aqueous media. To overcome such defects, some strategies have been suggested. For instance, simultaneous doping and usage of a suitable surface modifier changes the surface chemistry of ZnO.

This chapter reviews the tailoring characteristics of ZnO through doping and surface modification. Synthesis is described with emphasis on the hydrothermal technique. The importance of organic pollutants such as azo dyes and industrial pollutants are discussed. We also review the characterization of nanomaterials, using for example powder X-ray diffraction, Fourier transmission infrared spectra, scanning electron microscopy, zeta potential, UV-Vis spectroscopy, and dynamic light scattering. Moreover, different intrinsic and extrinsic parameter affecting fabrication and application of nanomaterials are explained in detail.

Keywords Doping • Nanomaterials • Photodegradation • Sunlight • Bandgap energy • Dyes • Characterization • Hydrothermal • Surface modification • Catalyst

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1.1 Introduction

Recently, zinc oxide (ZnO) has attracted much attention within the scientific community as a 'future material'. This is however, somewhat of a misnomer, as ZnO has been widely studied since 1935 (Bunn 1935), with much of our current industry and day-to-day lives critically reliant upon this compound. The renewed interest in this material has arisen out of the development of growth technologies for the fabrication of high quality single crystals and epitaxial layers, allowing for the realization of ZnO-based electronic and optoelectronic devices.

With a wide bandgap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO will be important for blue and ultra-violet optical devices (Wahab et al. 2013). Other favorable aspects of ZnO include its broad chemistry leading to many opportunities for wet chemical etching, low power threshold for optical pumping, radiation hardness and biocompatibility. Together, these properties of ZnO make it an ideal candidate for a variety of devices ranging from sensors through to ultra-violet laser diodes and nanotechnology-based devices such as displays.

As fervent research into ZnO continues, difficulties such as the fabrication of p-type ZnO that have so far stalled the development of devices are being overcome (Tsukazaki et al. 2005). We are thus moving ever closer to the future in which ZnO will be a viable and integral part of many functional and exotic devices.

1.2 Crystal Structure and Lattice Parameters

Zinc oxide crystallizes in three forms: hexagonal Wurtzite, cubic Zincblende, and the rarely observed cubic Rocksalt. The wurtzite structure (Fig. 1.1) is most stable at ambient conditions, belonging to the space group P6$_3$*mc* and is characterized by

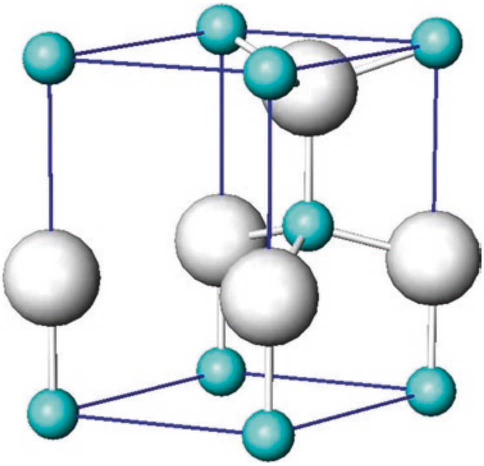


Fig. 1.1 ZnO wurtzite, also called B4 type structure

two interconnecting sublattices of Zn^{2+} and O^{2-}, such that each Zn ion is surrounded by a tetrahedral of O ions and vice-versa and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral. The rocksalt (NaCl-type) structure is only observed at relatively high pressures about 10 GPa (Özgür et al. 2005).

Hexagonal and zincblende polymorphs have no inversion symmetry. This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zincblende ZnO, and in pyroelectricity of hexagonal ZnO.

Aside from causing the inherent polarity in the ZnO crystal, the tetrahedral coordination of this compound is also a common indicator of sp^3 covalent bonding. However, the Zn-O bond also possesses very strong ionic character, and thus ZnO lies on the borderline between being classed as a covalent and ionic compound, with an iconicity of $f_i = 0.616$ on the Phillips iconicity scale (Phillips 1973). The lattice parameters of the hexagonal unit cell are $a = 3.2495$ Å and $c = 5.2069$ Å, and the density is 5.605 g/cm^3 (Lide 2002).

1.3 Properties of ZnO

1.3.1 Mechanical Properties

Table 1.1 gives a brief overview of the well-accepted and experimentally useful parameters describing the mechanical properties of ZnO. Slip bands along the basal planes which give rise to so called ‘pop-in’ events during indentation (Rössler 1969) loading can also be clearly seen.

ZnO is a relatively soft material with approximate hardness of 4.5 on the Mohs scale (Bloom and Ortenburger 1973). Its elastic constants are smaller than those of relevant III–V semiconductors, such as GaN. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnO are beneficial for ceramics (Vaithianathan et al. 2005).

Table 1.1 Important parameters for the alloy semiconductors $Zn_{(1-x)}Mg_xO$ and $Zn_{(1-y)}Cd_yO$

Parameter	$Zn_{(1-x)}Mg_xO$	$Zn_{(1-y)}Cd_yO$
Typical energy range (eV)	3.37–4.0	2.9–3.37
Maximum percentage alloy incorporation	43 %	70 %
a-axis length expansion (Å)	$3.250 + 0.036x$	$3.252 + 0.143y - 0.147y^2$
a-axis length expansion (Å)	$3.34 - 0.063x$	$5.204 + 0.956y - 5.42y^2$
Eg (eV)	$3.37 + 2.51x$	$3.29 - 4.40y + 5.93y^2$
$\Delta E_c/\Delta E_v$	70/30	–

Battez et al. (2008)

Among the tetrahedrally bonded semiconductors, it is reported that ZnO has the highest piezoelectric tensor (Özgür et al. 2005). This property makes it a technologically important material for many piezoelectrical applications, which require a large electromechanical coupling (Coleman et al. 2005).

1.3.2 Lattice Dynamics

In single crystal wurtzite ZnO, there are four atoms per unit cell, giving rise to 12 phonon modes. These modes are important for understanding the thermal, electrical, and optical properties of the crystal, and are as follows: one longitudinal-acoustic (LA), two transverse-acoustic (TA), three longitudinal-optical (LO) and six transverse-optical (TO) branches. The phonon modes of ZnO have been extensively studied and modeled (Meyer et al. 2004). Table 1.2 gives a list of the experimental values for the most common phonon modes visible at 300 K.

1.3.3 Thermal Properties

The thermal properties of wurtzite ZnO includes the thermal expansion coefficients, which are $a_a = 4.31 \times 10^{-6}$ K^{-1} and $a_c = 2.49 \times 10^{-6}$ K^{-1} at 300 K (Florescu et al. 2002); thermal conductivity, which falls in the range of $\kappa = 0.6\text{–}1$ W cm^{-1} K^{-1} (Look et al. 2004); and specific heat, which at constant pressure is $C_p = 40.3$ J mol^{-1} K^{-1} (Lide 2002).

1.4 Applications of ZnO

As mentioned previously, ZnO is already widely used in our society, and indeed, it is a key element in many industrial manufacturing processes. The applications of zinc oxide powder are numerous, and the principal ones are summarized below. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. For material science applications, zinc oxide has high refractive index,

Table 1.2 Experimentally determined principal phonon modes of wurtzite ZnO at 300 K

Phonon mode	Value (cm^{-1})
E_2^{low}	101
E_2^{high}	437
TO (A1)	380
LO (A1)	574
TO (E1)	591

Adachi (2005)

good thermal, binding, antibacterial, and photocatalytic properties. Consequently, it is added into various materials and products, including plastics, ceramics, glass, cement, rubber, lubricants (Rössler 1969), paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants, etc. (Colinge and Colinge 2005).

Thus, ZnO whilst already possessing a wide application base, has enormous opportunities for society and industry alike due to its unique properties, which are now being explored and applied. ZnO is an alternative for TiO_2 as a photocatalyst. There are many published papers on application of ZnO nanoparticles in environmental issues such as photodegradation of highly toxic and organic dyes, industrial wastewaters, agricultural effluents, air pollutants, and water treatment (Shahmoradi et al. 2010a, b, 2011a, b, 2013; Maleki and Shahmoradi 2012).

1.5 Energy Bandgap of ZnO

The measurement of the bandgap of materials is important in the metal oxide semiconductors, nanomaterials, and solar industries. The term "bandgap" refers to the energy difference between the top of the valence band to the bottom of the conduction band (Fig. 1.2); electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the bandgap energy.

Measuring the bandgap is important in the semiconductor and nanomaterial industries. The bandgap energy of insulators is large (>4 eV), but lower for semiconductors (<3 eV). The bandgap properties of a semiconductor can be controlled by using different metal oxide semiconductors such as WO_3, MnO_2, In_2O_3, Nd_2O_3, Fe_3O_4, NiO, and MoO_3. Table 1.3 shows Bandgap energies and corresponding radiation wavelength required for the excitation of some of metal oxide semiconductors.

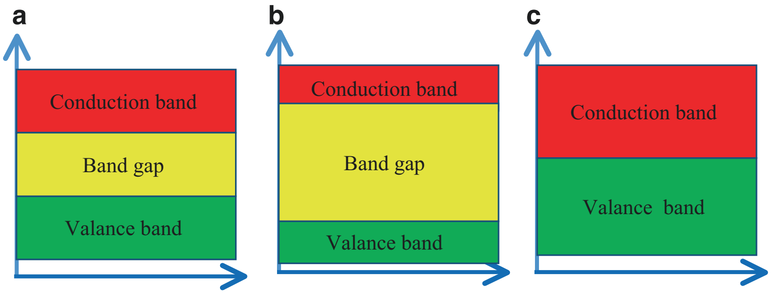


Fig. 1.2 Bandgap energy in (**a**) semiconductor, (**b**) insulator, and (**c**) conductor

Table 1.3 Bandgap energies and corresponding radiation wavelength required for the excitation of various semiconductor metal oxides

Semiconductor	Bandgap energy (eV)	Wavelength (nm)
ZnO	3.2	388
WO_3	2.8	443
MnO_2	0.58–0.7	213–177
In_2O_3	2.6–3.6	476–344
Nd_2O_3	5.8	213
MoO_3	3.1	399

Makino et al. (2001) and Duffy et al. (2000)

1.5.1 Opportunities for Bandgap Engineering

For a semiconductor to be useful, particularly in reference to photocatalysis; bandgap engineering is a crucial step in increasing photodegradation efficiency. By alloying the starting semiconductor with another material of different bandgap, the bandgap of the resultant alloy material can be fine-tuned, thus affecting the wavelength of exciton emissions. In the case of ZnO, alloying with WO_3, MnO_2, Nd_2O_3, In_2O_3, Fe_3O_4, NiO, and MoO_3 is an effective means of changing the energy bandgap (Shahmoradi et al. 2010a, b, 2011a, b, 2013; Maleki and Shahmoradi 2012).

1.6 Photocatalytic Applications of ZnO Nanomaterials

ZnO was used as a photocatalyst for degradation of organic molecules in aqueous solutions for the first time in 1970s (Zhang et al. 1998). Mostly, it is used in a powder form. The powder is suspended in aqueous solution of pollutant and the slurry is then irradiated. There are various techniques to improve optical properties, control morphology, and crystal size of the nanomaterials fabricated.

1.6.1 Pure ZnO Nanomaterials

As the size of ZnO particles decreases, the fraction of atoms located at the surface increases with higher surface area to volume ratios, which can further enhance the catalytic activity. The increase in the bandgap energy with decreasing nanoparticles size can potentially enhance the redox potential of the valence band holes and the conduction band electrons, allowing photoredox reactions, which might not otherwise proceed in bulk materials, to occur readily. One disadvantage of these nanoparticles is that they can only use a small percentage of sunlight for photocatalysis. Practically, there exists an optimal size for a specific photocatalytic reaction.

Solubility of zincite in basic hydrothermal solvents was studied and it was found that it could be solved in almost all of the solvents (Sobczyński and Dobosz 2001). There are many research works on synthesis and photocatalytic application of pure ZnO under UV light irradiation (Behnajady et al. 2009; Martin et al. 1994).

1.6.1.1 Problems in the Photocatalytic Application of ZnO Nanomaterials

It was mentioned that nanomaterials could be used in a wide range of applications, but there are some problems, which should be resolved to enhance the efficiency and performance of nanomaterials in their practical applications. These problems will be discussed in detail in the following subsections.

Aggregation of Nanomaterials

Behavior of particles in the nanosize scale differs from particles in a pile of bulk sample. Surface energy of particles in nanoscale increases extremely, and results in tendency of nanoparticles to aggregate and agglomerate.

It is difficult to break down aggregation of nanoparticles to be in the size of individual particles, and it essentially defeats the purpose of producing high surface area and small size particles. Now, it has been cleared that in large number of applications it is important not only to have individual size but also small particles less than 100 nm are desired. Therefore, it is required to find out an effective method to overcome this problem.

Poor Dispersion of Nanomaterials in Solvents

Poor dispersion of nanoparticles in solvents is another problem, which should be solved because in some applications like photodegradation, perfect dispersed nanoparticles are required.

Aggregation between nanoparticles leads to worse dispersion and particles in solvent after a while precipitate at the bottom of the medium. Thus, it is necessary to define a new strategy and method that can resolve those mentioned problems. It means on one side it prevents aggregation between nanoparticles and on the other side perfect dispersion of particles can be guaranteed. In addition, it is worth mentioning that as perfect dispersion of inorganic nanoparticles in solvents needs change surface properties of particles to hydrophobic, then, it is necessary to control surface of nanoparticles by organic modifiers and make new generation of advanced materials so-called inorganic-organic hybrid nanoparticles. Because of these reasons, surface modification of nanoparticles is propounded.

1.6.2 Metal Oxide Doped ZnO Nanomaterials

Over the past decades, metal-doped ZnO nanomaterials have been widely studied for improved photocatalytic performance on the degradation of various organic pollutants, i.e., under visible light irradiation. The limitation of the rate of photocatalytic degradation is attributed to the recombination of photogenerated electron-hole (e^--h^+) pairs. Various attempts have been made to reduce e^{-}–h^+ recombination in photocatalytic processes. These studies include doping metal ions into the photocatalyst lattice and coupling semiconductors (Behnajady et al. 2007).

The presence of metal ion dopants in the ZnO matrix significantly influences the charge carrier recombination rates and interfacial electron-transfer rates. The photoreactivity of doped ZnO appeared to be a complex function of the dopant concentration, the energy level of dopants within the nanoparticle lattice, their electronic configurations, the distribution of dopants, the electron donor concentrations, and the light intensity (Kometani et al. 2008).

1.6.3 Nonmetal Doped ZnO Nanomaterials

Nonmetal-doped ZnO nanomaterials have been regarded as the third generation photocatalysts. Various nonmetal-doped nanomaterials have been widely studied for their visible light photocatalytic activities. Nonmetal-doped ZnO nanomaterials have been demonstrated to have improved photocatalytic activities compared to those for pure ZnO nanomaterials, especially in the visible light region (Xu et al. 2015).

1.6.4 In Situ *Surface Modified ZnO Nanomaterials*

Surface modification of nanomaterials is somewhat new technique to tailor morphology, particle size, and other required properties of the nanomaterials fabricated. Surfactant, organic ligands, or capping agents are synonyms, which are used for surface modifiers. There are verities of surface modifiers, which can be applied *in situ* to modify and change surface chemistry of the ZnO nanomaterials fabricated. Caprylic acid and *n*-butylamine were used as surface modifier to fabricate desired configuration of ZnO nanoparticles. Surface modifiers can bring about reduction of particle size and agglomeration (Shahmoradi et al. 2010a, b, 2011a, b, 2013; Maleki and Shahmoradi 2012).

1.6.5 In Situ *Surface Modified Metal Oxide Doped ZnO Hybrid Nanomaterials*

Pure ZnO nanoparticles can use only small percentage (3–5 %) of sun light for photocatalysis, therefore, doping with suitable dopant can make shift from UV to visible region. Thus, photodegradation efficiency can be significantly increased. The *in situ* surface modification along with doping is a completely new technique, which was adopted in the author research works. Simultaneous usage of surfactant and dopant to modify ZnO nanomaterials could increase the photodegradation efficiency of industrial effluents and dyes due to changing morphology, shifting absorption region from UV to visible light, reducing particle size, etc. (Shahmoradi et al. 2010a, b).

1.7 Hydrothermal Technology for Synthesis Metal Oxide Doped ZnO Hybrid Nanomaterials

There are various methods adopted for fabrication of nanomaterials including chemical precipitation, super critical fluid, sol-gel, microemulsion, and hydrothermal technique. The latter is becoming one of the most important tools for advanced materials processing, particularly owing to its advantages in the processing of nanostructural materials for a wide variety of technological applications such as electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical, biophotonics, etc. The hydrothermal technique not only helps in processing monodispersed and highly homogeneous nanoparticles, but also acts as one of the most attractive techniques for processing nano-hybrid and nanocomposite materials. The term '*hydrothermal*' is purely of geological origin. It was first used by the British geologist, Sir Roderick Murchison (1792–1871) to describe the action of water at elevated temperature and pressure, in bringing about changes in the earth's crust leading to the formation of various rocks and minerals. It is well known that the largest single crystal formed in nature (beryl crystal of >1000 g) and some of the large quantity of single crystals created by man in one experimental run (quartz crystals of several 1000 s of g) are both of hydrothermal origin (Byrappa and Adschiri 2007).

In the recent years, with the increasing awareness of both environmental safety and the need for best energy utilization, there is chase for developing nonhazardous materials. Moreover, processing methods such as fabrication, manipulation, treatment, reuse, recycling of waste materials should be environmentally friendly. In this respect, the hydrothermal technique occupies a unique place in modern science and technology.

The term hydrothermal usually is defined as "any heterogeneous or homogenous chemical reaction in the presence of a solvent (whether aqueous or nonaqueous) above room temperature and at pressure greater than one atmosphere in a closed system" (Adschiri and Byrappa 2009). In nanotechnology, hydrothermal processing has an edge over the other conventional processes. It facilitates the issues like simplicity, cost effectiveness, energy saving, use of large volume of equipment (scale up process), better nucleation control, pollution free (since the reaction is carried out in a closed system), higher dispersion, higher rate of reaction, better shape control, and lower temperature operation in the presence of an appropriate solvent, etc. The hydrothermal technique has a lot of other advantages like it accelerates interactions between solid and fluid species, phase pure and homogeneous materials can be achieved, reaction kinetics can be enhanced, the hydrothermal fluids offer higher diffusivity, low viscosity, facilitate mass transport and higher dissolving power. Most important is that the chemical environment can be suitably tailored.

1.7.1 Factors Affecting Hydrothermal Fabrication of Surface Modified ZnO Nanomaterials

There are some important factors affecting size, morphology, optical property, purity, yield, etc. of the surface modified nanomaterials fabricated. The main important ones are solvent, precursor, temperature, pressure, running time, pH, and surface modifier. These factors will be explained in the following subsections.

1.7.1.1 Solvent

In any hydrothermal system or reaction, the role played by the solvent under the action of temperature and pressure is very important. Many workers have interpreted it in various ways (Yoshimura and Suda 1994). A variety of aqueous and nonaqueous solutions were tried to suit the preparation of a particular compound. Selection of a proper solvent mainly depends upon the precursor's solubility. Some precursors are soluble in water, while some of them are soluble in acidic or basic medium. ZnO along with the metal oxide dopants are soluble in acidic or basic medium. However, KOH and NaOH are most suitable candidate as solvent for fabrication of surface modified nanoparticles because using acid as solvent may result in obtaining impure or unwanted target compound while doping with metal oxides.

1.7.1.2 Precursors

Precursors are the raw materials, which can be considered as the foundation of the synthesizing process. Selection of proper precursor depends on the materials, which we are interested in its fabrication. The hydrothermal technique can be heterogeneous or homogenous reaction depending upon precursors and solvent. Here, the heterogeneous reaction has been adopted for fabrication of the surface modified metal oxide doped hybrid nanomaterials because the selected solvents are liquid and the main precursors are ZnO, different metal oxides as dopants.

1.7.1.3 Temperature

Temperature plays critical role in hydrothermal reactions. Some of the chemicals do not involve in chemical reactions at room temperature or in some cases, the temperature should be in a certain range. This factor can be controlled by changing the pressure applied. Since the mild hydrothermal conditions have been selected for nanomaterials fabrication, temperature was fixed in the range of 100–250 °C, which is mainly based on the boiling and melting points of the surfactants used.

1.7.1.4 Pressure

Hydrothermal reactions are taken place in a closed system, (i.e. $P =$ autogenous) so that the pressure could be controlled by changing the liner fill percentage. Earlier works indicate that 40–60 % filling results in good crystallinity (Byrappa et al. 2006).

1.7.1.5 Time Duration

Some of the chemical reactions are slow and under certain temperature and pressure, it takes time for materials to give chemical reactions. Some researchers have synthesized ZnO nanomaterials within 24–48 h and even more running time. However, the running time was reduced to only 8 h in the author research works (Shahmoradi et al. 2010a, b).

1.7.1.6 Surface Modifier

Surface modifiers, surfactant, capping agents, or organic ligands are applied on nanomaterials for adding functional groups, which change the surface chemistry of the nanomaterials fabricated. A suitable surfactant should be cost-effective, eco-friendly, low toxic, having density less than washing agent while recovering nanomaterials fabricated, etc. Based on these requirements, *n*-butylamine and caprylic acid were selected as surface modifier for *in situ* surface modification of metal oxide doped ZnO hybrid nanoparticles. Table 1.4 shows some of the main characteristics of these surface modifiers.

Table 1.4 Main characteristics of *n*-butylamine and caprylic acid

	Surface modifier	
Properties	*n*-butylamine	Caprylic acid
Synouname	NBA, 1-Butylamine	C8:0, octanoic acid
Density	0.74 g/cm^3, liquid	0.910 g/cm^3
Boiling point	77 °C, 350 K	237 °C, 510 K
Melting point	−49 °C, 224 K	16.7 °C
Molar mass	$C_4H_{11}N$	$C_8H_{16}O_2$
Molecular weigth	73.14 g mol^{-1}	144.21 g/mol
pKa	12.5	4.89
Solubility	Miscible/miscible	6.31 M in metanol
Viscosity	0.5 mPa.s at 20 °C	–

1.7.2 Hydrothermal Experimental Methodology

In the hydrothermal experiment, the starting precursors are taken in the Teflon liner in a definite molar proportion. The liner is closed tightly and placed inside the autoclave. A stainless steel washer is placed on the upper portion of the liner and then the cap of the autoclave provided with a spring system inside (to hold the liner tightly) is used to close the autoclave tightly. Finally, the autoclave assembly is placed inside the oven at a desired temperature over a definite period of time (experimental duration). The product in Teflon liner was then transferred to a clean beaker, washed with double distilled water, and later allowed the product to settle down. The surplus solution was removed using a syringe and the remnants were centrifuged for 20 min at 3000 rpm. The product was recovered and dried in a hot air oven at 40–50 °C for a few hours (Fig. 1.3).

1.7.2.1 Fabrication of Surface Modified Metal Oxide Doped ZnO Hybrid Nanomaterials

Doped ZnO hybrid nanoparticles were fabricated under mild hydrothermal conditions i.e., T = 100–250 °C and P = autogeneous. 1 M of pure ZnO was taken as starting material and the dopant (WO_3, MnO_2, MoO_3, Nd_2O_3 and In_2O_3%) was added into it. About 10 ml 1 N NaOH/KOH was added as a mineralizer to the precursor. At the same time different concentrations (0.8, 1, 1.2, 1.4 and 1.6 M) of *n*-butylamine and caprylic acid was added to the above mentioned mixture and it was stirred vigorously for a few minutes. The final mixture was then transferred into a Teflon liner (V_{fill} = 50 %), which was later placed inside a General-Purpose autoclave. The assembled autoclave was then kept in an oven with a temperature programmer-controller for 8 h. The temperature was kept at 100–250 C; i.e., 100 °C when

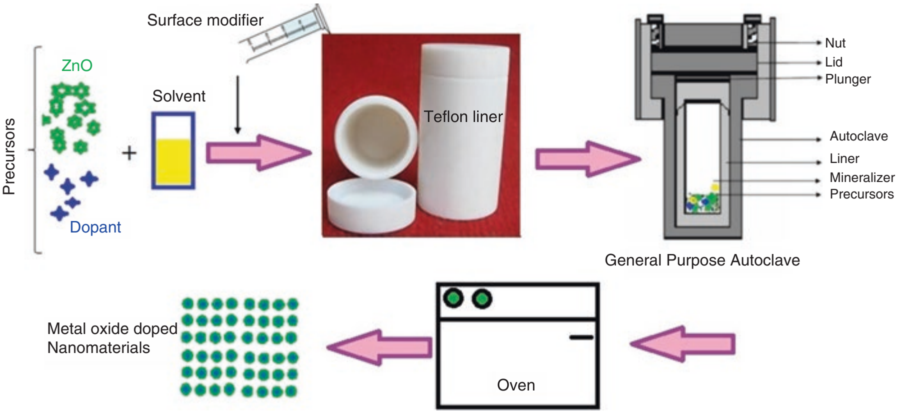


Fig. 1.3 Flowchart of hydrothermal fabrication of nanomaterials

n-butylamine was used as surface modifier and 250 °C when caprylic acid was used. After the completion of the experimental run, the autoclave was cooled to the room temperature. Then the product inside the Teflon liner was transferred into a clean beaker, washed with double distilled water, and later allowed the product to settle down. The surplus solution was removed using a syringe, the remnants were centrifuged for 10 min at 2000 rpm and this washing cycle was repeated thrice in order to remove the excess surfactant and solvent. The product was recovered and dried in a hot air oven at 40–50 °C for a few hours.

1.8 Characterization of Surface Modified Metal Oxide Doped ZnO Hybrid Nanomaterials

1.8.1 Powder X-Ray Diffraction (XRD) of Surface Modified Metal Oxide Doped ZnO Nanomaterials

Figure 1.4 shows the powder XRD data of unmodified pure ZnO, and surface modified ZnO nanoparticles using *n*-butylamine and caprylic acid. As this figure indicates, there is a small new peak, which is corresponded to caprylic acid (Ranade and Harrison 1981); it reveals that the caprylic acid has formed a complex with ZnO nanoparticles so that the structure has little bit changed. Such effect can be seen in all of the following plots, where caprylic acid has been used as surface modifier. However, the XRD data reveal a highly crystallized wurtzite structure (Figs. 1.5 and 1.6). There is a slight change in the lattice parameters of metal oxide doped ZnO hybrid nanoparticles at *a*-axis and *c*-axis when compared to pure ZnO, this confirms

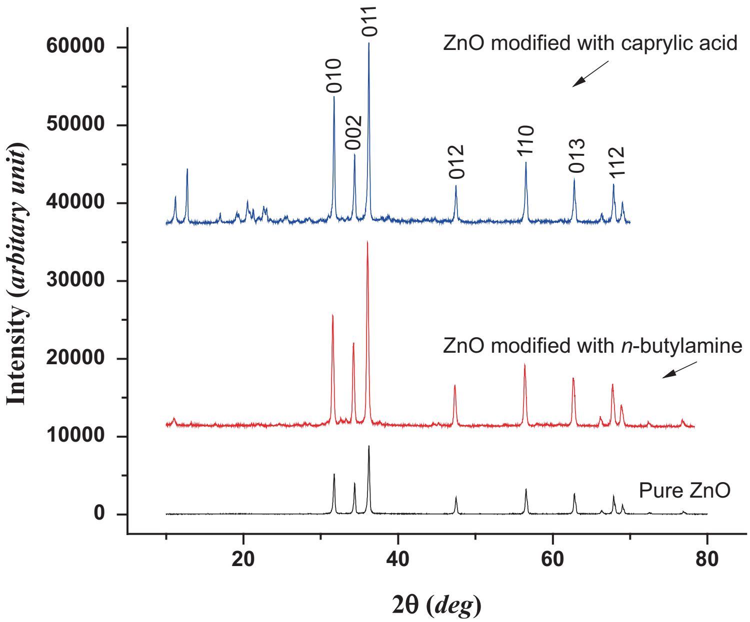


Fig. 1.4 Effect of surface modifier on the structure of ZnO nanoparticles could be observed in the Powder X-ray diffraction (XRD) patterns of surface modified ZnO nanoparticles

the existence of dopant atoms in ZnO hybrid nanoparticles (here only XRD plots of tungsten and manganese doped ZnO hybrid nanomaterials are presented). The powder XRD pattern of metal oxides doped ZnO hybrid nanoparticles shows seven primary peaks, which can be attributed to different diffraction planes of ZnO (Chen et al. 2004). Using improper solvent can also change the crystal structure. Effect of improper solvent on the crystal structure can be easily seen in Fig. 1.7. Temperature plays a critical role in fabricating of nanomaterials, especially in hydrothermal technique. Proper surface modification of nanomaterials could not occur at room temperature (Fig. 1.8).

1.8.2 FTIR of Surface Modified Metal Oxides Doped ZnO Hybrid Nanomaterials

The functional groups present in the modified nanoparticles can be studied using FTIR Spectroscopy. Figure 1.9 shows FTIR spectra of the unmodified reagent grade ZnO and surface modified ZnO hybrid nanoparticles using caprylic acid and *n*-butylamine. Here, no dopant has been applied. As this figure indicates, there is a

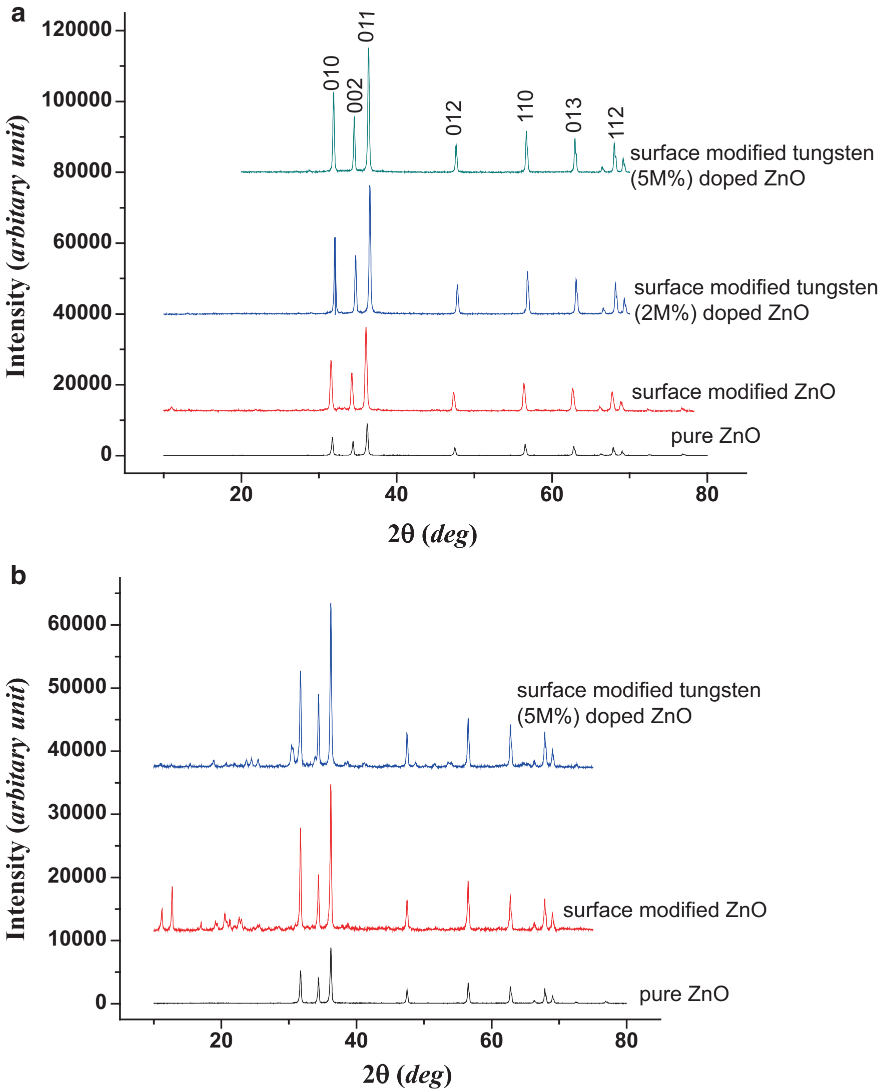


Fig. 1.5 Powder XRD patterns of surface modified tungsten doped ZnO nanoparticles using (**a**) *n*-butylamine and (**b**) caprylic acid as surface modifier. Notice appearance of new peaks in XRD of the *n*-butylamine modified nanoparticles

broad stretching bond around 3500 cm^{-1}, which corresponds to OH. This functional group was appeared when *n*-butylamine was used as surface modifier, such effect could not be observed in the case of surface modification of ZnO nanoparticles using caprylic acid. It can be concluded that modification of ZnO nanoparticles with *n*-butylamine will give OH stretching bond. Figures 1.10, 1.11 and 1.12 show the

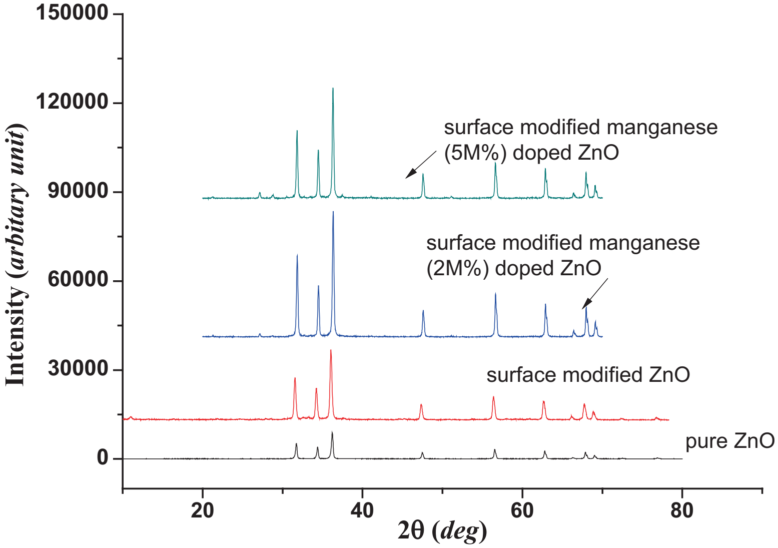
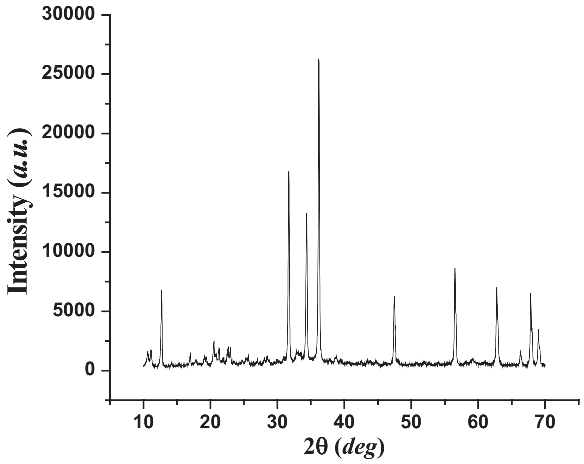


Fig. 1.6 Powder XRD patterns of surface modified manganese doped ZnO nanoparticles using *n*-butylamine as surface modifier. Notice that l

Fig. 1.7 Powder XRD patterns of surface modified ZnO nanoparticles using HCl as solvent



FTIR spectra of the reagent grade ZnO, surface modified undoped ZnO and metal oxide doped ZnO nanoparticles modified with *n*-butylamine and caprylic acid as surface modifier respectively. The FTIR spectra of the modified hybrid nanoparticles show the presence of new peaks imply that the reagents were chemically immobilized on the surface of nanoparticles.

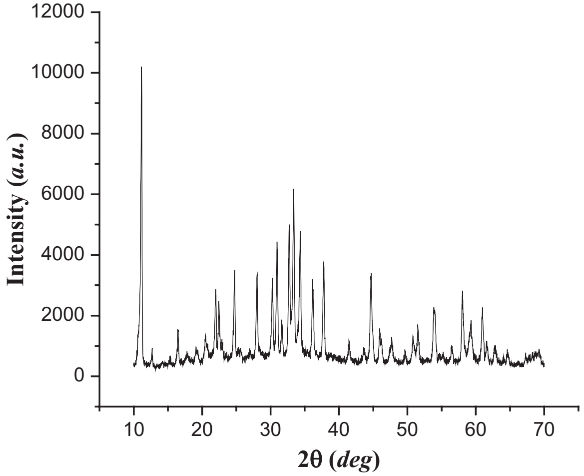


Fig. 1.8 Powder XRD patterns of surface modified ZnO nanoparticles using caprylic acid as surface modifier at room temperature

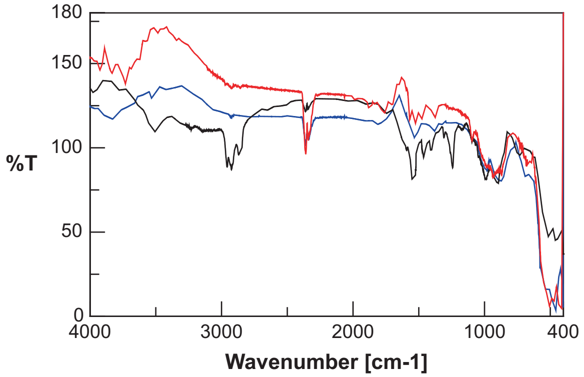


Fig. 1.9 FTIR spectra of 🟦 reagent grade ZnO, surface modified undoped ZnO hybrid nanoparticles using ⬛ caprylic acid, and 🟥 *n*-butylamine

1.8.3 Scanning Electron Microscopy (SEM) of the Surface Modified Metal Oxides Doped ZnO Hybrid Nanomaterials

The following images (Figs. 1.13 and 1.14) are the characteristic SEM of the surface modified metal oxide doped hybrid ZnO nanomaterials fabricated in the present work. The morphology of the surface modified metal oxide doped ZnO hybrid nanomaterials is different in each case and it may be due to the effect of doping and surface modification. These images reveal that the using surfactant along with proper solvent and dopant has reduced the morphology of the nanomaterials fabricated. Selecting improper solvent and non-stiocometric taking precursors can bring about agglomeration, amorphous particles, non-crystallinity and increasing size as it has been shown in Fig. 1.15.

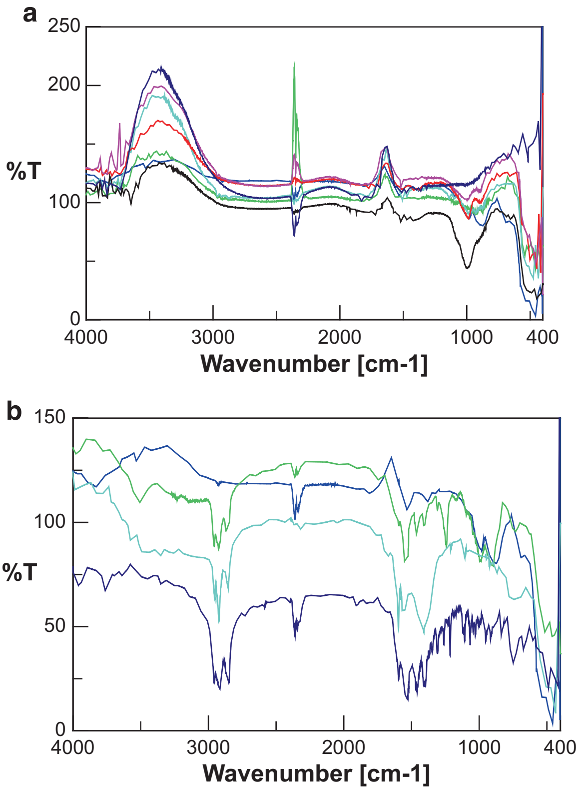


Fig. 1.10 FTIR spectra of ▬ reagent grade ZnO, ▬ modified undoped ZnO hybrid nanoparticles, ▬ 2 M% tungsten doped ZnO hybrid nanoparticles modified with 0.8 M surfactant, ▬ 2 M% tungsten doped ZnO hybrid nanoparticles modified with 1.0 M surfactant, ▬ 2 M% tungsten doped ZnO hybrid nanoparticles modified with 1.2 M surfactant, ▬ 2 M% tungsten doped ZnO hybrid nanoparticles modified with 1.4 M and ▬ 2 M% tungsten doped ZnO hybrid nanoparticles modified with 1.6 M (**a**) *n*-butylamine and (**b**) caprylic acid

1.8.4 *Bandgap Energy Studies of Surface Modified Metal Oxide Doped ZnO Nanomaterials*

As it was explained earlier, the bandgap energy of the nanomaterials fabricated could be measured using UV-Vis spectrophotometer. The following graphs (Fig. 1.16) show the effect of surfactant and dopant on bandgap changes. Figure 1.15 clearly demonstrates that tungsten oxide doped ZnO hybrid nanomaterials have smaller bandgap energy compared with pure ZnO, which make them very efficient under sunlight irradiation for photodegradation processes.

1.8.5 *Zeta Potential of Surface Modified ZnO Nanomaterials*

Zeta (ζ) potential measurement was performed for surface modified ZnO nanoparticles in order to characterize the surface charge of nanoparticles and Fig. 1.17 shows the result as a function of *pH*. The obtained ζ potential of the nanoparticles

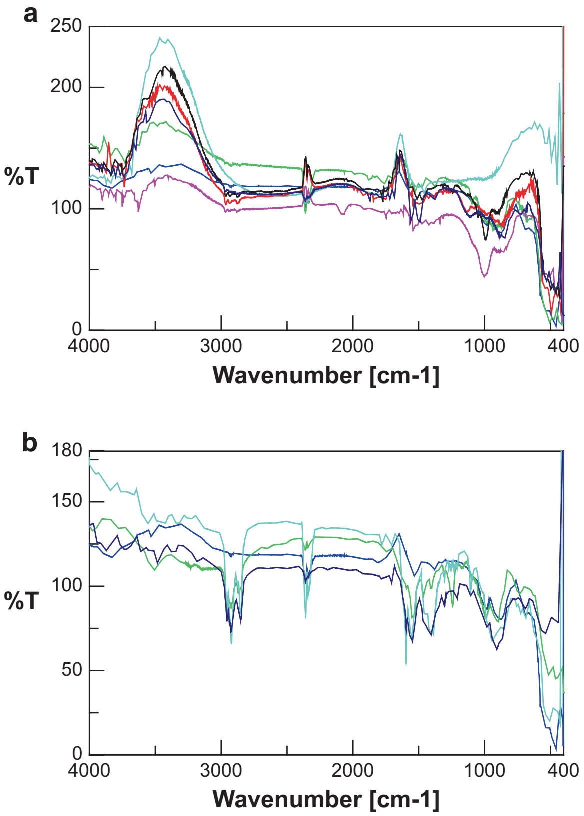


Fig. 1.11 FTIR spectra of ▬ reagent grade ZnO, ▬ modified undoped ZnO hybrid nanoparticles, ▬ 5 M% tungsten doped ZnO hybrid nanoparticles modified with 0.8 M surfactant, ▬ 5 M% tungsten doped ZnO hybrid nanoparticles modified with 1.0 M surfactant, ▬ 5 M% tungsten doped ZnO hybrid nanoparticles modified with 1.2 M surfactant, ▬ 5 M% tungsten doped ZnO hybrid nanoparticles modified with 1.4 M and ▬ 5 M% tungsten doped ZnO hybrid nanoparticles modified with 1.6 M (**a**) *n*-butylamine and (**b**) caprylic acid

was found to decrease with increase of *pH* as is expected for a surface with acid-base group. The iso-electric point or point of zero charge (PZC) for ZnO nanoparticles was found to be 4.0 and 4.2 for modification by caprylic acid and *n*-butylamine respectively. For small enough nanoparticles, a high ζ potential will confer stability, i.e. the solution or dispersion will resist aggregation. When the potential is low attraction exceeds repulsion and the dispersion will break and flocculate. Therefore, colloids with high ζ potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate. Our results indicate that the both surface modified ZnO hybrid nanoparticles are stable and highly negatively charged (at pH > 4.0–4.2) and this negative charge intensity is proportional to the increasing *pH*. On the other hand, the particles fabricated are positively charged at pH < 4.0. The modified nanoparticles synthesized had low agglomeration, which prevents their flocculation or coagulation tendency (Shahmoradi et al. 2010a, b).

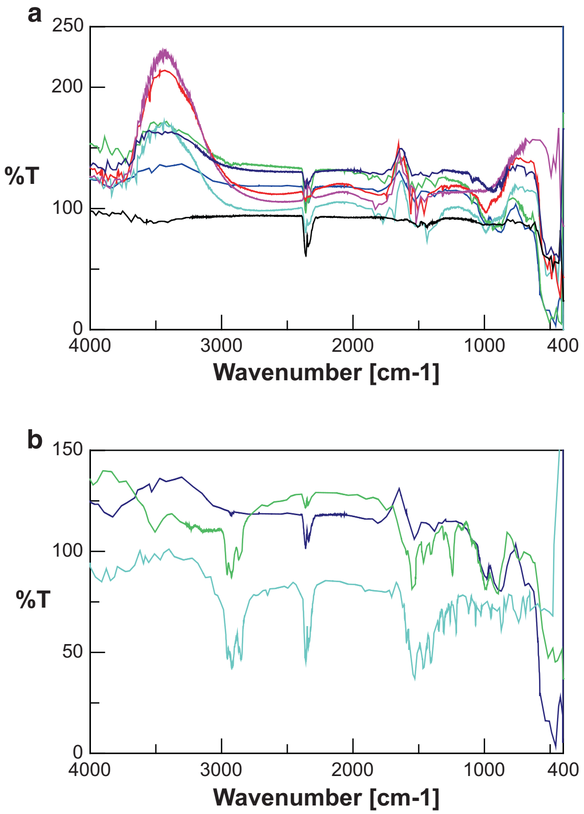


Fig. 1.12 FTIR spectra of ▬ reagent grade ZnO, ▬ modified undoped ZnO hybrid nanoparticles, ▬ 2 M% manganese doped ZnO hybrid nanoparticles modified with 0.8 M surfactant, ▬ 2 M% manganese doped ZnO hybrid nanoparticles modified with 1.0 M surfactant, ▬ 2 M% manganese doped ZnO hybrid nanoparticles modified with 1.2 M surfactant, ▬ 2 M% manganese doped ZnO hybrid nanoparticles modified with 1.4 M and ▬ 2 M% manganese doped ZnO hybrid nanoparticles modified with 1.6 M (**a**) *n*-butylamine and (**b**) caprylic acid

1.9 Factors Affecting the Photocatalytic Process

Photocatalytic reactions are extremely complex processes involving many participants namely water, organic substrate, catalyst, light, and oxygen. Therefore, it is obvious that operational parameters related to each of these agents may affect the efficiency of the photocatalytic process. Photocatalytic reaction rates are known to be affected by several operation conditions including *pH* of the medium, catalyst loading, substrate concentration, light intensity (photonic flux), temperature, and oxygen pressure. In addition, physical and chemical intrinsic properties of the photocatalyst may affect its photoefficiency.

Nanomaterial crystal composition, surface area, crystallite dimensions, and presence of surface hydroxyl groups are known to be important intrinsic parameters that influence the efficiency of the catalyst in photocatalytic reactions. Since these themes will be the subject of some of the studies presented in this chapter, they will be discussed in detail in the next sections. However, a brief description of the effect caused by each extrinsic parameter in the efficiency of the photocatalytic process is described in the following.

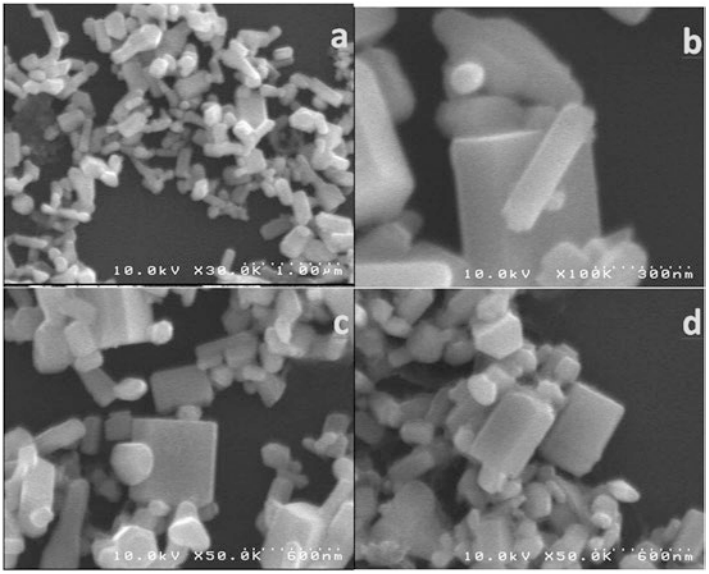


Fig. 1.13 Characteristic Scanning Electron Microscopy (SEM) images of surface modified 5 M% tungsten doped ZnO nanoparticles using 1.0 M (**a** and **b**) n-butylamine and (**c** and **d**) caprylic acid

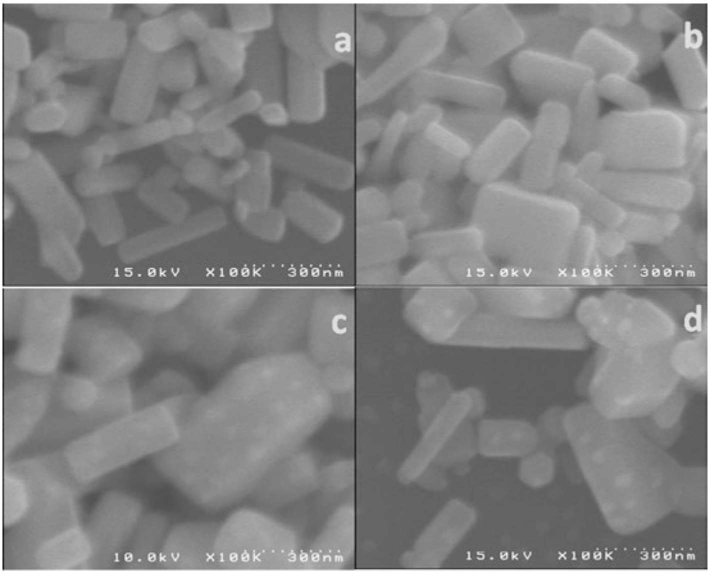


Fig. 1.14 Characteristic SEM images of surface modified 5 M% manganese doped ZnO nanoparticles using 1.0 M (**a** and **b**) n-butylamine and (**c** and **d**) caprylic acid

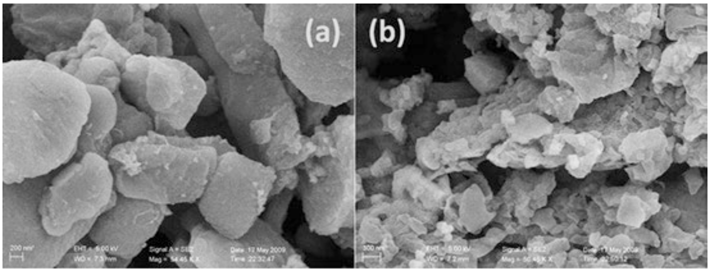
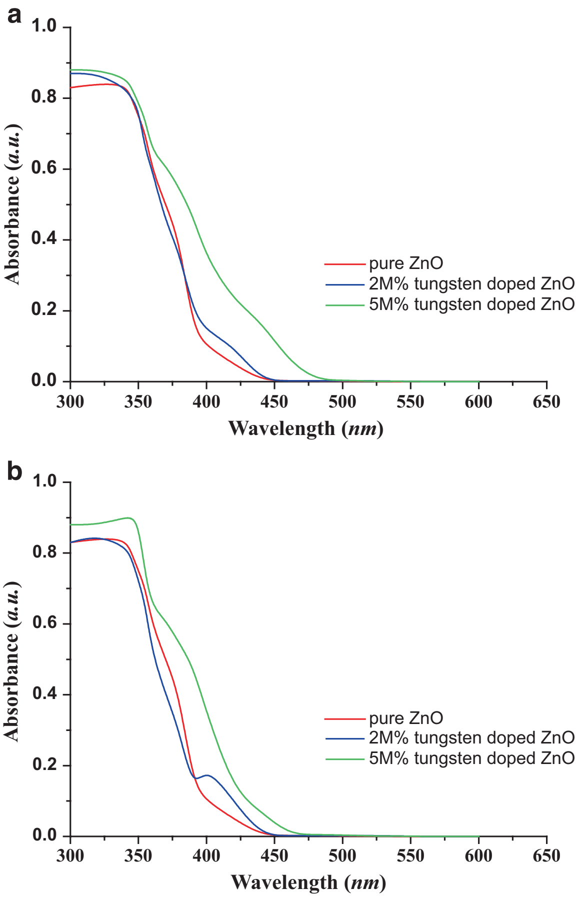


Fig. 1.15 Characteristic High Resolution Scanning Electron Microscopy images of surface modified ZnO nanoparticles using HCl as solvent and (**a**) n-butylamine and (**b**) caprylic acid as surfactant

Fig. 1.16 Effect of doping on bandgap energy of the modified tungsten doped ZnO nanoparticles modified with (**a**) caprylic acidand (**b**) *n*-butylamine



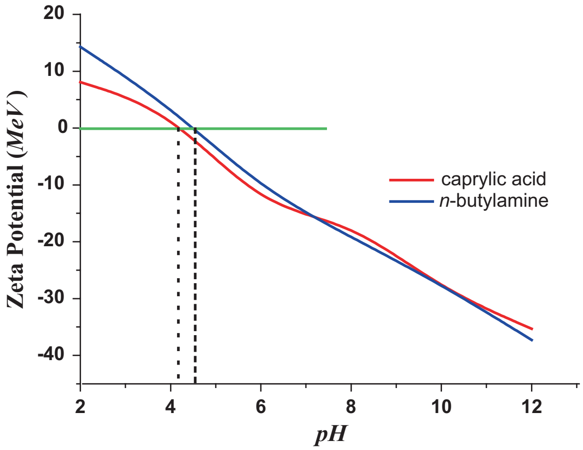


Fig. 1.17 Zeta potential of surface modified ZnO nanoparticles

1.9.1 Catalyst Loading

In slurry photocatalytic process, catalyst dosage is an important parameter. Photocatalytic degradation of 2 mg/L BBF and Amaranth dye was carried out with modified tungsten (2 M%; 5 M%) doped ZnO hybrid nanoparticles and reagent grade ZnO catalyst loading of 0–2.0 g/L under the UV and sun light- irradiation, respectively. The process of the degradation of these dyes as a function of fabricated ZnO nanoparticles and pure ZnO dosage is presented in Fig. 1.18.

As shown in the Fig. 1.18, in the absence of ZnO, the removal percentage of these dyes is almost zero. The addition of nanoparticles enhances the removal of both contaminants with different speed. The removal rate of these contaminants increases as the concentration of the dyes thickens. It should be mentioned that there was no difference in the extent of degradation based on the light source in the case of reagent grade ZnO but as this figure indicates, the degradation also occurred in visible light, which confirms the effect of doping on photodegradation of these dyes. An optimal result was achieved at a ZnO dosage of 1.6 g/L. The removal decreases with a further increase in the catalyst dosage.

1.9.2 Substrate Concentration

In photocatalytic degradation reactions, the observed rate constant decreases with the increase of initial organic pollutant concentration. The main steps of the photocatalytic reaction occur on the surface of the catalyst, and therefore, a high adsorption capacity is associated with reaction favoring. A further increase of the concentration does not affect the actual catalyst surface concentration, and therefore, this may result in a decrease of the rate constant observed.

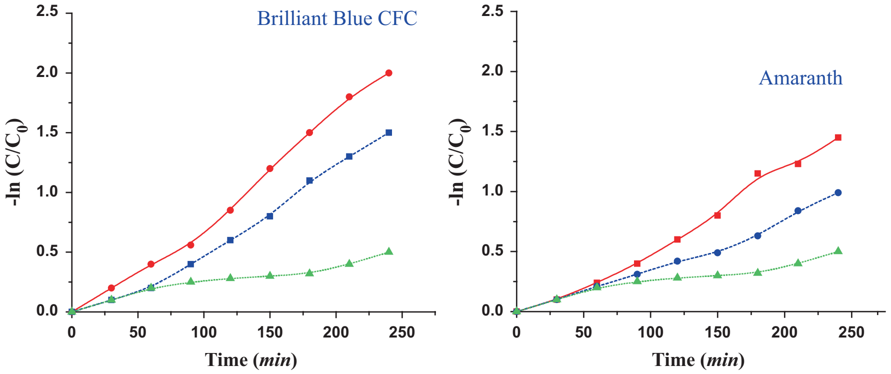
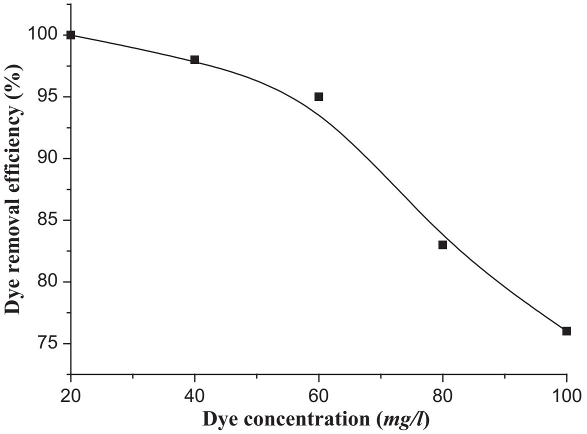


Fig. 1.18 Photodegradation of Brilliant Blue FCF and Amaranth dye using 🟥 5 M% tungsten doped; 🟦 2 M% tungsten doped ZnO nanoparticles modified with *n*-butylamine and 🟩 reagent grade ZnO (Shahmoradi et al. 2011b)

Fig. 1.19 Effect of dye concentration on solar degradation efficiency (Maleki and Shahmoradi 2012)



The effect of dye concentration on solar degradation efficiency was evaluated through conducting experiments using different concentrations (20–100 mg/L) of DB 71. Figure 1.19 shows that the greater the dye concentration, the less efficient the solar degradation. It can be noted that increasing dye concentration prohibits light penetration; hence, the degradation efficiency would reduce.

1.9.3 *Effect of Light Source*

Figure 1.20 shows the comparison of photodegradation of BBF and Amaranth dyes at different moment in the presence of modified tungsten (2 M%; 5 M%) doped ZnO hybrid nanoparticles under sun light and UV irradiation. The photodegradation ratio

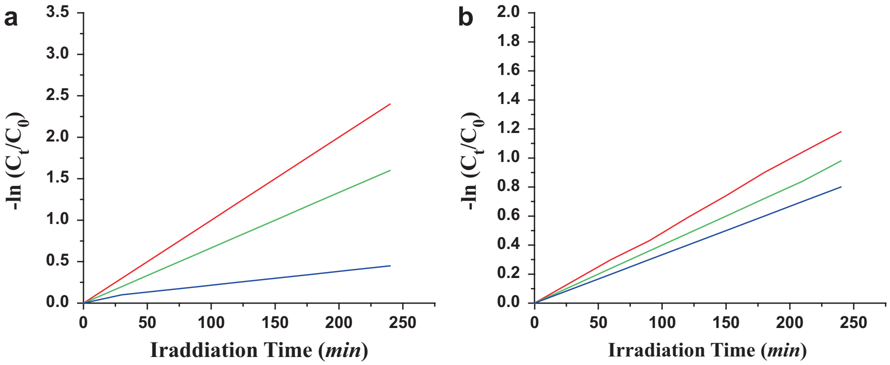


Fig. 1.20 Effect of light source: (**a**) sun light and (**b**) UV light on photodegradation of Amaranth using 🟥 5 M% tungsten doped; 🟩 2 M% tungsten doped ZnO nanoparticles modified with *n*-butylamine and 🟦 reagent grade ZnO (Shahmoradi et al. 2011b)

in the presence of modified nanoparticles increases along with irradiation time and attains about 84.21 % and 60.23 %, respectively, within 3.0 h sunlight irradiation. In the case of UV irradiation, the efficiency is 62.35 and 38.70 %. The results indicate the photocatalytic degradation reaction is pseudo-first-order kinetic reaction.

1.9.4 pH of the Medium

The pKa value of BBF is 5.63, 6.58, which means that the pH has an effect on its photodegradation. The pH was adjusted using varying concentrations of 0.02 N HCl or NH_4OH. The effect of pH is shown in Fig. 1.21. The maximum efficiency was observed at extreme basic conditions. The change in pH of the solution varies with the dissociation of the dye molecule and the surface properties of the nanoparticles used. The initial adsorption of the dye molecules onto the nanoparticles greatly depends on the solution pH. Increase in the degradation efficiency under the alkaline condition could be attributed to the increase in hydroxyl ions, which induce more hydroxyl radical formation.

1.9.5 Effect of Surfactant Concentration on Photocatalytic Degradation

There are a variety of organic ligands, which can be applied for surface modification of ZnO, CdS and other particles. We found that despite non-toxicity, eco-friendly, suitable melting point, etc., density and its concentration play a critical role in its suitability. The density of surfactant should be less than water and the precursors otherwise; its removal from the nanoparticles prepared will be very difficult.

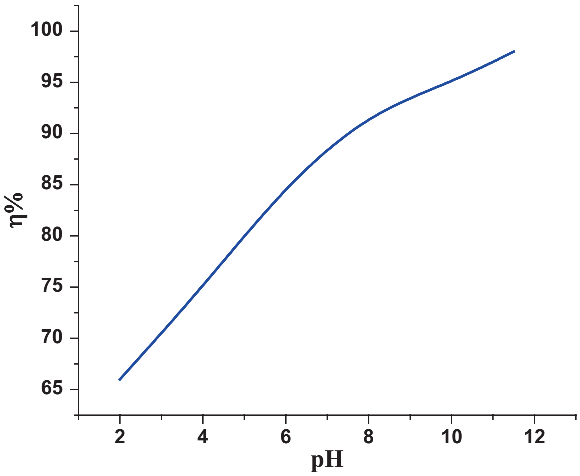


Fig. 1.21 Effect of pH on photodegradation of Brilliant Blue FCF dye (Shahmoradi et al. 2011b)

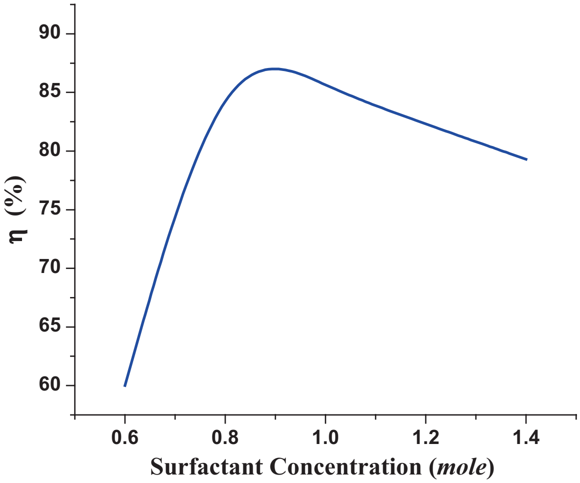


Fig. 1.22 Relationship between concentrations of surfactant (*n*-butylamine) applied to modify surface of doped ZnO nanoparticles and photodegradation efficiency (Shahmoradi et al. 2013)

Figure 1.22 shows effect of surfactant concentration on photodegradation of effluents. As it indicates the optimum concentration of the surfactant is found to be 0.8 M for *in-situ* modification of the tungsten ZnO hybrid nanoparticles. Higher concentration of surfactant in the nutrient might give desired morphology and particle size, but it will bring about over coverage of the nanoparticles synthesized. Therefore, the incident light does not induce the photocatalysts due to the heavy coverage and bonding of hybrid nanoparticles. It should be mentioned that along with surfactant there are many factors, which affect the morphology and particle size of the synthesized nanoparticles.

1.10 Conclusion

The present research work highlights the fabrication, and characterization of highly efficient surface modified metal oxide doped hybrid nanomaterials under mild hydrothermal conditions. The application of these surface modified metal oxide doped hybrid nanomaterials have been deeply studied in the degradation of some selected dyes and industrial effluents under different experimental conditions.

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Chapter 2
Nanomaterials: Classification, Biological Synthesis and Characterization

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Abstract Nanomaterial research has recently gained importance due to prospective applications in human life and environment. However, scientific research on nano- and micro-sized materials has reached a saturation state. As a result, researchers planning to further develop nanomaterials, need an outlook on recent advances in synthesis, classification and characterization of nanomaterials. There is a need in particular for an overview of synthesis using biological materials namely bacteria, fungi, yeast, and plants, in order to design eco-friendly nanomaterials. Methods used to characterize these synthesized nanoparticles must also be reviewed to suggest the appropriate techniques in terms of spectroscopic and microscopic methods to study the physio-chemical properties of nanomaterials. Here we review the nature, types and synthesis of nanomaterials, with a detailed evaluation on biological synthesis. We also discuss in detail nanoparticle production by microorganisms including bacteria, fungi and yeasts. This chapter also provides updates on currently available techniques used to characterize nanoparticles.

Keywords Nanomaterial classification • Synthesis methods • Nanoparticle characterization • Microscopy

2.1 Introduction

Nanomaterials or nanoparticles represent a significant aspect of nanotechnology which deals with various studies involving particles ranging between 1 and 100 nm at least in one spatial dimension (Schneider 1997). Though several research groups

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have showed interest in nanotechnology in the recent years, their primary motivations regarding nanomaterials were towards its unique electronic, optical and mechanical properties compared to their bulk counterpart and molecular components. Production of nanoscale materials on a large scale is usually very difficult which has led to its synthesis and studies made solely in the lab scale conditions and later tried to be scaled-up for commercial purposes. Though nanotechnology has a high impact on many field of sciences including physics, engineering, biology, agriculture and food sciences, its importance in the agri-food sector is gaining momentum. Several government agencies of developing and developed countries are actively involved in research and development of nanomaterials in Agri-food sector owing to its importance in serving the growing demand for improved quality of common foods mainly food and water. The major scopes of agri-food based nanotechnology research is towards develop of functional food, effecient and rapid delivery of drugs, nutrients and gene functions at cellular level in plants and animals during stress (Nair et al. 2010), nano array based technology for detection and contamination of foods by pathogen (Senturk et al. 2013), nanocomposite or nanobiocomposite based plastic film coatings in food packaging (Arora and Padua 2010), nanoemulsion based material for decontamination of equipments and food packing (Chaudhry et al. 2008; McClements and Rao 2011), nanoparticles for effective increase and direct delivery of nutrients into the cells (Acosta 2009).

In all of these requisite or ongoing areas of nantoechnology research, the production of innovative and enhanced materials can be achieved by either top-down or bottom-up approach which are two approaches for the synthesis of nanomaterials. In the top-down approach, nanoscale devices are created by using larger, externally-controlled devices to direct their assembly. The top-down approach often makes use of traditional workshop or microfabrication methods in which externally-controlled tools are used to cut, mill and shape materials into the desired shape and order. Attrition and milling for making nanoparticles are typical top-down processes. In the bottom-up approach, molecular components arrange themselves into more complex assemblies like atom-by-atom, molecule-by-molecule and cluster-by-cluster from the bottom (e.g., growth of a crystal). Synthesis of nanoparticles by colloid dispersions is an example of the bottom-up approach. The bottom-up approach generally produces nanostructures with fewer defects as compared to nanostructures produced by the top-down approach. An approach where both these techniques are employed is known as an hybrid approach. Some of the materials commonly used for the synthesis of nanomaterials are outlined in Table 2.1.

In Agri-food industry, integration of nanoresearch is essential to select appropriate nanomaterials with desired chemical composition, controlled size, uniformity and stability. However, the common modes of synthesis of nanoparticles are by chemicals which are toxic to environment. Eco-friendly synthesis of nanoparticles is important keeping in mind its agricultural perspective. Extensive literature and database search reveals that several researchers in the field of nanoparticle synthesis and assembly have turned to the use of biological systems such as bacteria, yeasts, algae, fungi and actinomycetes, agricultural residues, biomass and plants. This chapter emphasizes on recent advances in synthesis, classification and characterization of

Table 2.1 Materials to be used for the synthesis of nanomaterials

Materials	Production methods	Applications
Carbon Fullerenes	Using two carbon electrodes in a helium or neon atmosphere and generated arc to results in formation of fullerenes	Targeted drug delivery (Vogelson 2001), Lubricants (Holister et al. 2003), catalysts (Nakamura and Sawamura 2001), Nano-scale chemical sponges (Tagmatarchis and Shinohara 2001).
Carbon nanotubes	Produced by three techniques such as carbon-arc discharge, laser ablation of carbon or chemical vapor deposition	Scanning probe microscopy (Rothschild et al. 1999), Antistatic materials (Garland 2009), Carbon nanotube-enhanced plastic (Garland 2009).
Metals	Several methods to fabricate materials such as combustion synthesis, mechanochemical processing, chemical precipitation, sol-gel processing, laser ablation, pyrolysis.	Wound dressings (Panacek et al. 2006), Electromagnetic interference/ radio frequency interference shielding (Yang et al. 2007)
Metal Oxides	Combustion synthesis, mechanochemical processing, chemical precipitation, sol-gel processing, laser ablation, pyrolysis.	Water and strain repellent textiles (Vigneshwaran et al. 2006), sunscreens (Jaroenworaluck et al. 2006).

nanoparticles synthesized using several biological materials namely bacteria, fungi, yeast, and plants and also summarizes the characterization techniques in terms of spectroscopic and microscopic methods to study the physio-chemical properties of nanomaterials.

2.2 Classification of Nanomaterials

Nanomaterials are broadly classified into three categories, namely Nanoparticles, Nanoclays, Nanoemulsions (Fig. 2.1).

2.2.1 Nanoparticles

Nanoparticles can exist as nanostructures or as composites. All nanostructures can be built from elementary units (blocks) having low dimensionality – zero dimension, one dimension, two dimensions and three dimensions (Table 2.2). Depending on the dimension in which the size effect on the resultant property becomes apparent and the nanomaterials can be classified as zero dimensional (quantum dots) in which the movement of electrons is confined in all three dimensions,

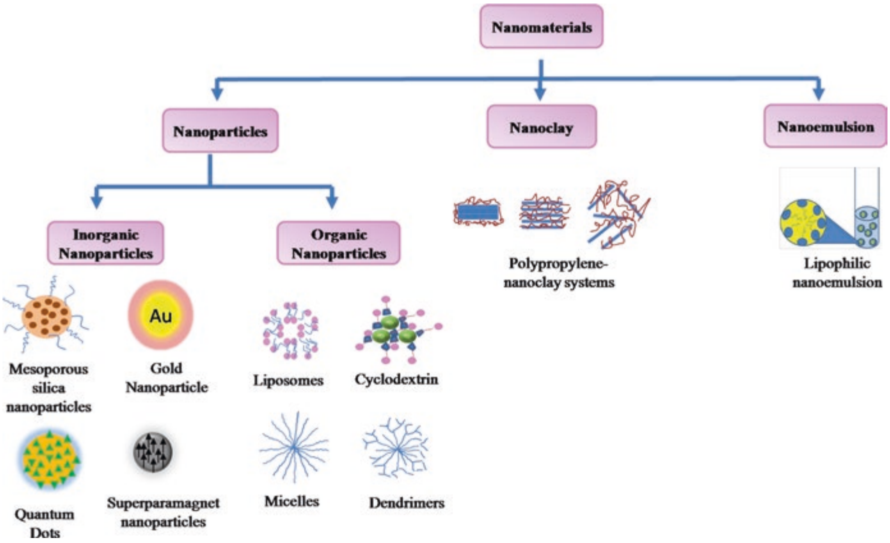

Fig. 2.1 Classification of nanomaterials: nanoparticles, nanoclays and nanoemulsions

Table 2.2 Different dimensions of nanomaterials with an examples

Elementary units	Examples
0D Units (3 dimensions in the monometric range)	Molecules, Clusters, fullerenes, rings, metal carbides, powders, grains.
1D Units (2 dimensions in the monometric range)	Nanotubes, fibres, filaments, whiskers, spirals, belts, springs, columns, needles
2D Units (1 dimensions in the monometric range)	Layers

one-dimensional (quantum wires) in which the electrons can move freely only in the X-direction, two-dimensional (thin films) in which case the free electrons can move in the X-Y plane, or three dimensional (nanostructured material built of nanoparticles as building blocks) in which the free electron can move in the X, Y and Z directions (Siegel 1993).

Nanocomposites are found as a microcrystal matrix (micro-nano type), in which nanometer sized particles or inclusions (spherical, fiber-like, plate-like) of a second phase are dispersed in the intergranular regions or in both inter/intra granular spaces of matrix grains. Based on matrix material, three categories of nanocomposites can be named such as ceramic matrix nanocomposite, metal matrix nanocomposite and polymer matrix nanocomposite. Table 2.3 represents the materials, methods and application of different nanocomposite in agri-food sector.

Further nanoparticles can also be classified into organic and inorganic nanoparticles based on nature of material fabrication. Inorganic nanoparticles are typically shaped by the precipitation of inorganic salts, which are interconnected with molecules by covalent, metallic and so forth. The organic nanoparticles were assembled

Table 2.3 Materials, methods and application of nanocomposite on agri-food sector

Nanocomposite	Materials	Methods	Application in Agri-food sector
Ceramic matrix nanocomposite	Al_2O_3/SiO_2, SiO_2/Ni, Al_2O_3/SiC, Al_2O_3/CNT	Powder process, Polymer precursor process, Sol-Gel process	Electrochemical determination of the food dyes, sunset yellow and tartrazine, in food and beverage samples (Gan et al. 2012).
			To prevent oil molecules from clumping together (Sekhon 2014).
			Used as antimicrobial agent in many products e.g. food preservation, disinfection of medical products and decontamination of materials (Kawahara et al. 2000; Matsumura et al. 2003).
Metal matrix nanocomposite	$Fe\text{-}Cr/Al_2O_3$, Ni/Al_2O_3, Co/Cr, Fe/MgO, Al/CNT, Mg/CNT	Spray pyrolysis, Liquid infiltration, Rapid solidification process, Sol-gel, colloidal process, RSP with ultrasonics, High energy ball milling	Used for long term food packaging (Azeredo 2009).
			Used as antimicrobial agents in food packaging and in some cases as food supplement (Chaudhry et al. 2008).
			Surfaces of refrigerators and storage containers are coated with silver nanoparticles to prevent growth of foodborne pathogens and food spoilage bacteria (Cho et al. 2005).
			Application in monitoring agricultural pollutants for the assessment of impacts of these pollutants on biological and ecological health and in increase of crop productivity and reducing land burden (Sekhon 2014).
			Enhancement of many physiological parameters such as enhanced photosynthetic activity and nitrogen metabolism in plants (Kole et al. 2013).

(continued)

Table 2.3 (continued)

Nanocomposite	Materials	Methods	Application in Agri-food sector
Polymer matrix nanocomposite	Poly vinyl alcohol (PVA), poly ethylene glycol (PEG), poly caprolactone (PCL), poly lactic-co-glycolic acid (PLGA), poly glycerol sebacate	Intercalation/ prepolymer from solution, In-situ intercalative polymerization, Melt intercalation, template synthesis, Sol-gel process	Packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, fruit juice and dairy products, beer and carbonated drinks bottles (Silvestre and Cimmino 2013).
			Useful for farmers to retain moisture and control weeds (Ray 2013).
			Help to control oxidation of food stuffs and to prevent the formation of off-flavors and undesirable textures of food (Lagarón et al. 2005).

themselves in three dimensional form. Self-assembly, the vicinity of zwitterionic particles, with polar and nonpolar areas, as the primary segments of nanoparticles was key element for the fabrication of organic nanoparticles. Organic nanoparticles are synthesized using natural and synthetic organic molecules such as lipid bodies, protein aggregates, milk emulsion and other complex structure (Viruses, etc.). This form of nanoparticles plays a provital role in agri-food sector and cosmetic industries. Several food material for example, creams, chocolate, and cakes present nanoemulsions in their definition. Synthesis of organic nanoparticles can be fabricated by either top-down or bottom-up approach. The most common techniques are mechanical milling, microfluidics and lithography by top-down method. Precipitation, condensation were used to produce organic nanoparticles by bottom-up method. Inorganic nanoparticles on the other hand are more stable than organic nanoparticles but are limited by their stability in terms of either chemical or mechanical and nature of particle. Produced nanoparticles mainly differed in their consistency, size, yield or crystallinity and are often synthesized using various methods (Emulsion-Solvent Evaporation Method, Solvent Displacement/Precipitation method, hydrothermal, microemulsion, polyol process and aerosol pyrolysis). These nanoparticles can be broadly classified into nanostructure and nanocomposites based on the arrangement and their structures with combination of other material such as polymer, etc.

2.2.2 Nanoclays

Preparation of nanoclays and organoclays using charged (hydrophilic) nature of clay molecules such as alkyl/aryl ammonium, phosphonium or imidazolium in aqueous or solid state. The ion exchange reaction has two consequences; first, the gap between the single sheets is widened, enabling organic cations chain to move in between them and second, the surface properties of each single sheet are changed from being hydrophilic to hydrophobic or organophilic. It is easy and simple to characterize the chemical composition of nanoclays by gravimetric analysis, inductive coupled plasma, X-ray diffraction and fourier transform infrared spectroscopy.

2.2.3 Nanoemulsion

Dispersion of polymer, droplets and solid material in the form of a viscous liquid leads to an interesting soft material. The dispersed phase is also known as internal phase or the discontinuous phase while the outer phase is called dispersion medium, external phase or continuous phase. The emulsifying agent is also known as intermediate or interphase. Nanoemulsion can be synthesized by two methods; high (ultrasonification, high pressure homogenization, microfluidizer) and low energy emulsification (phase inversion temperature, solvent displacement and phase inversion composition).

Properties and usefulness of nanoparticles has been proved to various aspects, including size, polydispersity, dimensions and stability of nanoparticles and biomolecules (proteins and poly nucleic acids). Nanoparticles are produced by three different methods such as chemical, physical and bio-based.

2.2.4 Synthesis of Nanoparticles

This chapter mainly discusses the chemical and physical methods of nanoparticle synthesis.

2.2.4.1 Chemical Synthesis Methods

Chemical methods for nanoparticle production have been straightforward in nature and often allow synthesis of nanoparticles in large quantities. Moreover the possibility of controlling particle size even at nanometer scale is also possible during chemical synthesis of nanoparticles (Hyeon 2003). These exist a wide variety of methods in chemical synthesis of nanoparticles which include reduction, co-precipitation, nucleation, sol–gel method, flow injection, electrochemical, solvothermal, hydrothermal and microwave-assisted (Yu et al. 2009; Anbarasu et al. 2015; Umer et al. 2012; Chaki et al. 2015). Several methods of chemical synthesis, the reagents used and conditions are mentioned in Table. 2.4.

Chemical Reduction

The most commonly used approach for synthesis of nanoparticles is chemical reduction of organic and inorganic reducing agents such as sodium citrate, ascorbate, sodium borohydride ($NaBH_4$), elemental hydrogen, polyol process, Tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol)-block copolymers. This synthesis process results in agglomeration forming colloidal nanoparticles. Usage of protective or capping agents such as poly vinyl alcohol, poly vinylpyrrolidone, poly ethylene glycol, poly methacrylic acid and polymethylmethacrylate in addition to presence surfactants groups namely thiols, amines, acids and alcohols will able to stabilize the particles from sedimentation, agglomeration, or losing their surface properties.

Microemulsion

Nanoparticles are produced by initial spatial separation between two immiscible phases (metal and reducing agent) in two-phase aqueous organic systems and the interface between the two phases is mediated by quaternary ammonium salt. Metal

Table 2.4 Chemical mediated synthesis of nanoparticles

Type of nanoparticle	Precursor	Reducer	Stabilizer	Particle size range (nm)	References
Silver	$AgNO_3$	$NaHB_4$	surfactin	3–28	Wiley et al. (2005)
Silver	$AgNO_3$	Dextrose	PVP	22±4.7	Merga et al. (2007)
Silver	$AgClO_4$	Ethylene glycol	–	17–70	Evanoff et al. (2004)
Copper	$CuSO_4.5H_2O$	Sodium borohydrate	SDS	2–10	Lisiecki et al. (1996)
Copper	$CuCl_2.2H_2O$	Ascorbic acid	Ascorbic acid	2	Xiong et al. (2011)
Copper	$Cu(NO_3)_2$	Hydrazine	PAA Na	20–100	Grouchko et al. (2009)
Fe_3O_4	$FeCl_3.6H_2O$ $FeCl_3.4H_2O$	Hexamethylenediamine	Polyethylene glycol	13–14.4	Anbarasu et al. (2015)
Fe_3O_4	$FeCl_3.6H_2O$	Sodium borohydrate	-	8	Chaki et al. (2015)

clusters in the interface are stabilized, mainly due to capping of stabilizer molecules in the non-polar aqueous medium and transferred to organic phase.

Sol-Gel Process

In this method, wide variety of materials can be used for the synthesis of nanoparticles in desired shapes (particles, fibers or films). Primarily, sol formation is carried out by dissolving the metal alkoxide, metal-organic, or metal-inorganic salt precursors in a suitable solvent. Upon drying the sol, a polymeric network is formed in which the solvent molecules are trapped inside a solid (gel). Subsequent drying of the gel followed by the calcinations and sintering leads to the final ceramic product.

Polymerization

It is a very common method for preparation of nanomaterials. During polymerization the formation of microemulsion is a very much important factor, which has been the focus of extensive research worldwide due to its importance in a variety of technological applications. These applications include enhanced oil recovery, combustion, cosmetics, pharmaceuticals, agriculture, metal cutting, lubrication, food, enzymatic catalysis, organic and bio-organic reactions, chemical synthesis of nanoparticles and nanocapsules etc.

Oxidation Process

Oxidizes or deoxidizes of raw nanomaterial in the liquid or quasi-liquid phase state. The oxidation phases can be used to prepare the nanoparticles of metals, alloys or oxides, in either water solutions or organic solutions.

UV-Initiated Photoreduction

UV-initiated photoreduction induced nanoparticles were synthesized in the presence of protective and stabilizing agents (citrate, polyvinylpyrrolidone, poly (acrylic acid), and collagen) at room temperature. Synthesis and growth of nanorods and dendrites mainly depends on concentration of polyvinyl alcohol and silver nitrate.

Microwave-Assisted Synthesis

It is a most promising technique over other conventional method (Oil bath) for synthesis of nanoparticles with smaller sizes, narrower size distributions, and a higher degree of crystallization. Microwave heating has shorter reaction times, reduced energy consumption, and a better product yield which prevents the agglomeration of the particles formed.

Sonochemical Processing

Implementation of high intensity ultrasound wave as energy source in respective sol material has initiated a new field in processing technology. It results in collapse of the bubbles of the sol and it leads to very high temperature, high pressure, high heating and cooling rate. The extreme conditions during acoustic wave enable the reactants to cross the activation energy barrier in a very short amount of time to form the product phase.

Irradiation Method

Simple and effective technique, wide variety of irradiation (visible to high) is used to synthesis of nanoparticles. Irradiation of light source in an aqueous solution of silver salt and surfactant can produce silver NPs with a well defined shape and size distribution.

Electric Dispersion Reaction

The technique involves subjecting the reactor liquid (metal-alkoxide solution) to a pluse electric field and results in a precipitation reaction to synthesize ultra fine precursor powders of advanced ceramic materials. Under the applied electric field, the sol is shattered to micron-sized droplets, termed as microreactors, which contain hydrous precursor precipitate. The formed precursor powders can be thermally processed to obtain oxide nanoparticles.

2.2.4.2 Physical Method

Evaporation-condensation, Combustion synthesis, Arc discharge/plasma, Laser/electron beam heating, Laser ablation technique are the most prominent physical methods for the synthesizing of nanoparticles. Main advantage over chemical method is devoid of solvents and uniform distribution of nanoparticles.

Evaporation-Condensation

It is a technique evaporation of metals, alloys and ceramics using gases and allows reacting with each other. Later it condensed using cool gases results in the formation of nanoparticles or nanocapsules. It has many disadvantages; tube furnace occupies a large space, consumes a great amount of energy while raising the environmental temperature around the source material, and requires a lot of time to achieve thermal stability.

Combustion Synthesis

The major advantage of the method is that it is fast and required the least external energy input and gives high output with the possibility of producing wide variety of ceramic oxides. In combustion synthesis, there is the exploitation of an excess heat generating or exothermic reaction, to overcome the activation energy barrier for the formation of products using precursor organic compound (fuel) as the reducing agent and a metal salt as the oxidizing agent.

Arc Discharge/Plasma

This technique has been used widely for the synthesis of fullerenes and other related materials. There are two methods for the production of plasma; Direct current arc plasma and high frequency plasma. Direct current arc method is convert inert/active gases into ionized with the generation of high temperature and melt the materials. Further condensation of the evaporating matters lead to the formation of nanoparticles and nanocapsules.

Laser/Electron Beam Heating

Main principle of technique is to emit the electron from electron gun with high temperature due to application of high voltage and thus creates vacuum in the electron gun. Conveniently, using transmission electron microscope can be used for electron beam heating and irradiating of the materials for developing different form of nanomaterials such as carbon nanotubes, carbon nanocapsules, and carbon nanoparticles. It has several advantages like heating source is outside the evaporation system, any materials, including metals, compounds, ceramics, etc., there is no contamination from the heating source.

Laser Ablation Process

Laser ablation technique is recent development for the synthesis of nanoparticles in controlled particle size and compositions. The technique involves the vaporization of a target using pulsed laser, which is then followed by the controlled condensation in a diffusion cloud chamber under well-defined conditions of temperature and pressure. A wide variety of metal oxides, carbides and nitrides can be synthesized in nanoscale dimensions.

2.2.5 *Biological Synthesis of Nanoparticles*

Despite the presence of extensive preparation techniques, most of these methods have complex protocols, extreme conditions of temperatures and toxic chemicals as reducing agents which not only result in high running costs but may also contain minor toxic contaminations on particle surface which question their direct application in biological systems (Hebbalalu et al. 2013). Biological nanoparticle synthesis on the other hand, makes use of biological catalysts which result in an environment friendly approach of synthesis thereby gaining precedence over conventional physical or chemical methods (Kruis et al. 2000; Sastry et al. 2003; Ahmad et al. 2003; Hebbalalu et al. 2013). Several existing methods of biological nanoparticle synthesis are explained in detail below.

2.2.5.1 Plant Mediated Synthesis of Nanoparticles

Noruzi (2015) has comprehensively reviewed the biosynthesis of gold nanoparticle using plant extracts in which he has covered various methods of green synthesis of nanoparticles and their characterization techniques in detail

The review also covers application of gold nanoparticle in various fields. With this note, we are including some more recent research reports on synthesis of nanoparticle using plant extracts. Silver and gold nanoparticles synthesis has been reported extensively using Neem (*Azadirachta indica*) leaf broth (Shankar et al. 2004). *Chenopodium album* (an obnoxious weed) leaf extract used for the synthesis of silver and gold nanoparticle and produced quasi-spherical shaped particle with size of 10–30 nm and in the same study the influence of leaf extract quantities, metal ion concentration, contact time, temperature and pH on the synthesis of nanoparticles were also evaluated. With increase of concentration of the leaf extract, the size of the particle becomes small. The particle size was increased with increase in metal ion concentration. At 5 and 1 mM concentration, 40–90 nm silver nanoparticle was formed and 50–100 nm of gold nanoparticles was formed at 1 mM concentration. The reaction time resulting in synthesis of nanoparticle ranges from 15 min to 2 h and sharp peaks were obtained upto 2 h following which a slight variation was observed. On studying the effect of temperature and pH on silver nanoparticle synthesis, increase in temperature increased the particle size but large sized nanoparticle only in case of a lower pH. However in case of gold nanoparticle, almost similar shape and size was observed from pH4 to pH10. Flavanones and terpenoids present in the plant or leaf extracts often been reported to be responsible for the synthesis of nanoparticles. Oxalate and aldehydic groups present in the leaf can be act as reducing agent as well as ligand (Dwivedi and Gopal 2010).

Aluminium oxide nanoparticles were synthesized from lemon grass leaf extract in the size of 9–180 nm which were spherical in shape (Ansari et al. 2015). Similarly, Prabhu et al. 2015 demonstrated the extracellular synthesis of copper nanoparticles in the size of 20–25 nm using *Garcinia mangostana* leaf extract. *Garcinia man-*

gostana leaf extract also examined for the production of silver nanoparticle. The optimum reaction time in both cases was 1 h and 1 mM concentration of substrate for the synthesis of nanoparticle. Based on temperature, initial increase in temperature led to the formation of increase in number of particles and at higher pH, smaller sized particles were observed (Veerasamy et al. 2011).

Coleus amboinicus leaf extract produced spherical, triangular, truncated triangular, hexagonal and decahedral shaped gold nanoparticle with the size range of 4.6–55.1 nm. Aromatic amines, amides and secondary alcohols were reported to be responsible for the capping of the particle (Narayanan and Sakthivel 2010). *Magnolia kobus* and *Diopyros kaki* synthesized gold nanoparticle extracellularly, at lower temperature and decreased concentrations of leaf broths. They produced spherical, triangular, pentagonal and hexagonal nanoparticle in the size of 5–300 nm. At higher temperature and increase concentration of leaf broth, small spherical shaped nanoparticles were produced. gold nanoparticles synthesized using *Magnolia kobus* are bounded by some proteins and metabolites such as terpenoids having functional groups of amines, alcohols, ketones, aldehydes and carboxylic acids (Song et al. 2009). Similar results were observed in the synthesis of gold nanoparticle using olive leaf extract by Khalil et al. 2012. When *Zingiber officinale* extracts used, gold nanoparticles of size 5–15 nm were synthesized. Alkaloids, alkanoids, flavonoids in the extracts were reported to act as capping agents. The synthesized particles were used for blood biocompatibility (Kumar et al. 2011). These nanoparticles were non platelet activating and non-complement activating on contact with human blood. These nanoparticles are not aggregate with other blood cells.

Terminalia bellirica fruit extract have also been used to synthesize silver nanoparticle, and the nanoparticles evaluated for antibacterial and antioxidant activity. In their research, the authors have identified gallic acid to be responsible for the reduction and stability of the nanoparticles (Hoskote Anand and Mandal 2015). Further silver nanoparticle synthesis using beet root (Bindhu and Umadevi 2015) and *A. indicum* leaves extract have also been reported (Ashokkumar et al. 2015). The synthesized nanoparticles were spherical in shape and 10 nm in size. Gold nanoparticle production using cold and hot extract of *Pedalium murex* showed that both the extracts produced nanoparticles in the range of 180–200 nm. Hexagonal, triangular and spherical nanoparticle was seen in TEM analysis and semi-spherical nanoparticle was observed in SEM analysis (Peter et al. 2014).

In recent studies, seed extract of *Pistacia atlantica* was utilized for the synthesis of silver nanoparticle which produced spherical shaped particles with 27 nm in size. The particles were stable in the pH range of 7–11 and OH group acts as a reducing/capping agent (Sadeghi et al. 2015). In the same year, the same authors used the leaf extract of *Ziziphora tenuior* for the synthesis of silver nanoparticle which formed spherical particles with 8–40 nm size. The alkaloids, phenolic compounds, terpenoids and co-enzymes present in the leaf have been hypothesized to play a major role in the reduction and stabilization of the nanoparticles (Sadeghi and Gholamhoseinpoor 2015). When *Ficus carica* leaf extracts were used to synthesize silver nanoparticles irradiances between 6.5 and 13.3 mW/cm^2 in the range of 330–550 nm wavelength were used and the results were compared in the dark and under direct sunlight (Ulug et al. 2015). Available data on synthesis of nanoparticles using plant extract is represented in the Table 2.5.

2.2.5.2 Bacteria in Synthesis of Nanoparticle

Inorganic materials are produced by microbes either intra or extracellularly. Among microorganisms, bacteria have been extensively studied by researchers for the synthesis of metallic nanoparticles (Table 2.6). Bacteria can be cultivated in shorter intervals of time and are easy targets for the recovery of nanoparticles. Several researchers are working on the synthesis of nanomaterials for more than decades. Recent developments and current scenario of the nanoparticle research has been reviewed by many scientists. A comprehensive explanation of extracellular and intracellular silver nanoparticle synthesis of bacteria or bacterially derived components has been reported by Singh et al. 2015. They also proceed further and mention in detail, the mechanism behind the extra and intracellular synthesis, as well as the role of reducing as well as capping agents in the synthesis (Fig. 2.2).

Several bacterial strains, regardless of their taxonomic groups have been reported to synthesize silver nanoparticles (Mohanpuria et al. 2008; Narayanan and Sakthivel 2010; Sweet et al. 2012). On a careful observation, it can be understood that most of these isolates are soil and marine origin, thus they were involved in several biogeochemical cycles of metals (Sweet et al. 2012). These bacteria are metabolically accustomed to presence of metals in their environment and detoxify them by reduction and/or precipitation mechanism of inorganic ions to metal nanoclusters (Narayanan and Sakthivel 2010). Strain *Pseudomonas stutzeri* AG259 which was primarily isolated from silver mines showed synthesis of silver nanoparticles and magnetotactic bacteria *Magnetospirillum magneticum* produced magnetic (Fe_3O_4) nanoparticles (Mohanpuria and Rana 2008). However there are also a few reports where strains of *Lactobacillus* sp., *Bacillus* sp., *Shewanella algae* and *Rhodobacter sphaeroides* are able to synthesize nanoparticles of metals such as gold, silver, titanium, platinum and zinc (Sweet et al. 2012). Therefore, one microorganism can form nanoparticles of different metals and the nanoparticle synthesizing capacity of a given bacterial strain dependent on the physiological properties of the strain but its lineage or taxonomic group to which they belong.

Until now, specific bacterial secretions responsible for bio-reduction of silver have not been reported, with the exception of a NADH dependent nitrate reductase that involved in microbial nanoparticle synthesis (Durán and Seabra 2012). Under conditions of high pH, EPS from bacteria, made of glucose, delivered reducing power to reduce metal ions into nanoparticles (Sintubin et al. 2009). However, in psychrotolerant bacteria, a direct evidence of proteins or EPS production promoting AgNPs synthesis at low temperatures remains to be documented. Interestingly, one psychrotolerant bacteria *Pseudoalteromonas antarctica* NF3, produced EPS and certain outer membrane vesicle proteins that were linked to survival of this bacteria under low temperature (Nevot et al. 2006a, b). Regardless of the putative carbohy-

Table 2.5 Plant-mediated synthesis of nanoparticles

Plant	Type of nanoparticle	Morphology	Size range (nm)	Location/ organelle	References
Azadirachta indica	Silver, Gold	Flat, plate (Gold nanoparticle) Spherical (Silver nanoparticle)	5–35	Leaf extract	Shankar et al. (2004)
Chenopodium album	Gold, Silver	Quasi-spherical	10–30	Extracellular	Dwivedi and Gopal (2010)
Lemon grass	Aluminum oxide	Spherical	9–180	Leaf extract	Ansari et al. (2015)
Garcinia mangostana	Copper	Spherical	20–25	Extracellular	Prabhu et al. (2015)
Garcinia mangostana	Silver	Spherical	35	Leaf extract	Veerasamy et al. (2011)
Coleus amboinicus	Gold	Spherical, triangle, truncated triangle, hexagonal and decahedral shaped	4.6–55.1	Extracellular	Narayanan and Sakthivel (2011)
Magnolia kobus and *Diopyros kaki*	Gold	Spherical, triangle, pentagons, hexagones	5–300	Leaf extract	Song et al. (2009)
Olive leaf	Gold	Spherical, triangle, pentagons, hexagones	5–300	Leaf extract	Khalil et al. (2012)
Zingiber officinale	Gold	Irregular	5–15	Intracellular	Kumar et al. (2011)
Terminalia bellirica	Silver	Spherical	20	Fruit extract	Hoskote Anand and Mandal (2015)
Beet root	Silver	Spherical	15	Beet root extract	Bindhu and Umadevi (2015)
A. indicum	Silver	Spherical	10	Leaf extract	Ashokkumar et al. (2015)
Pedalium murex	Gold	Hexagonal, triangular and spherical	180–200	Leaf extract	Peter et al. (2014)
Pistacia atlantica	Silver	Spherical	27	Seed extract	Sadeghi et al. (2015)
Ziziphora tenuior	Silver	Spherical	8–40	Leaf extract	Sadeghi and Gholamhoseinpoor (2015)
Ficus carica	Silver	Spherical	330–550	Leaf extract	Ulug et al. (2015)

Table 2.6 Bacterial-mediated nanoparticle synthesis

Bacteria	Type of nanoparticle	Morphology	Size range (nm)	Location/organelle	References
Pseudomonas stuzeri AG259	Silver	Triangular, hexagonal, spheroidal	200	Periplasmic space, Intracellular	Slawson et al. (1992)
Morganella sp. RP-42	Silver	Spherical	20–30	Extracellular	Parikh et al. (2008)
E.coli	Cadmium sulfide	Spherical, elliptical	2–5	Intracellular	Sweeney et al. (1998)
Clostridium thermoacetium	Cadmium sulfide	–	–	Cell surface, Extracellular	Cunningham and Lundie (1993)
Sulfate-reducing bacteria	Magnetite	–	20	Cell surface	Watson et al. (1999)
Actinobacter sp.	Magnetite	Quasi-spherical	10–40	Extracellular	Bharde et al. (2005)
Rhodopseudomonas capsulata	Iron Sulfide	pH7-spherical, pH-4 Triangular nanoplates	10–20	Extracellular	He et al. (2007)
Ureibacillus thermosphaericus	Silver	Spherical	10–100	Extracellular	Juibari et al. (2011)
Halomonas maura	MR(muran)/ CH(chitosan)	-	30–200	Polysaccharide	Raveendran et al. (2015)
Geobacillus stearothermophilus	Silver, Gold	Spherical	Gold nanoparticle –5–8, Silver nanoparticle – 5–35.	Extracellular	Mohammed Fayaz et al. (2011)
Shewanella oneidensis	Gold	Spherical	2–50	Cell membrane, Extracellular	Suresh et al. (2011)
Bacillus subtilis	Titanium Oxide	Spherical	10–30	Intracellular	Dhandapani et al. (2012)
Marinobacter pelagius,	Gold	Spherical and triangles	10	Intracellular	Sharma et al. (2012)
Arthrobacter nitroguajacolicus	Gold	Spherical	40	Intra- extracellular	Dehnad et al. (2015)
Saccharophagus degradans	Manganese oxide	Hexagonal and spherical	35	Extracellular	Salunke et al. (2015)

Halococcus salifodinae BK3	Tellurium	Hexagonal needle shaped	10	Intracellular	Srivastava et al. (2013)
E. coli	Gold	Spherical	10	Intracellular	Gholami-Shabani et al. (2015)
Pseudomonas mandelii	Silver	Spherical	1.9–14.1	Extracellular	Mageswari et al. (2015)
Psychrophilic bacteria	Silver	Spherical	6–13	Extracellular	Shivaji et al. (2011)

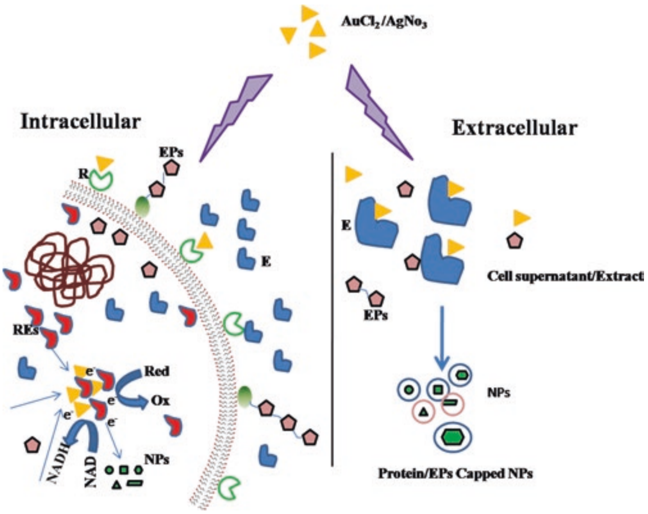

Fig. 2.2 Mechanism for synthesis of intracellular and extracellular nanoparticles by microorganisms. *EP* Exopolysaccharide, *R* Receptor, *E* Enzyme, *RE* Reducing enzymes, e^- Electron

drate and protein based mechanisms, specific cellular proteins or polymers based AgNP synthesis remains unclear at present (Sintubin et al. 2009; Shivaji et al. 2011).

The techniques involved in the characterization and application of nanoparticle have also been illustrated extensively in the past (Fedlheim and Foss 2001; Oskam 2006). As bacterial synthesis of nanoparticle has been described in detail by so many authors, in this chapter, we have tried to emphasize synthesis of nanoparticles by extremophilic bacteria as well bacteria colonizing niche environments. One of the primary reports on nanoparticle synthesis by extremophilic bacteria was on *Pseudomonas stuzeri* AG259. The bacterium was able to synthesize silver nanoparticles of size 35–46 nm intracellularly and accumulate the synthesized particles in its periplasmic space (Slawson et al. 1992). *Morganella* sp. RP-42, an insect midgut bacterium produced extracellular silver nanoparticle of size 20±5 nm and was identified to host three homologous silver resistant gene (*sil*E, *sil*P and *sil*S) in its plasmids. The gene *Sil*E was found to encode a periplasmic silver-binding protein (Parikh et al. 2008).

In other studies, cadmium sulfide (CdS) nanocrystals were produced intracellularly by *E. coli* (Sweeney et al. 1998) and extracellularly at the cell surface by *Clostridium thermoacetium* (Cunningham and Lundie 1993). In a study by Watson et al. 1999, Magnetic iron sulfide (FeS) nanoparticles of size about 20 nm were observed on the cell surface of sulfate-reducing bacteria. Though FeS nanoparticles are commonly found to be synthesized under anaerobic condition, a later study showed FeS nanoparticle production by *Actinobacter* sp. under aerobic conditions (Bharde et al. 2005). In another report, Konishi et al. (2004) demonstrated the effect of pH in influencing the size of nanoparticles. Under pH 1, the extracellularlly synthesized particles were 50–500 nm in size whereas at pH7 there was significant size reduction upto 10–20 nm. Similar results were observed in *Rhodopseudomonas capsulate*. Moreover nanoparticle synthesis at pH 7 was found to result in more spherical shaped particles with size ranging from 10 to 20 nm whereas at pH 4, triangular nanoplates were observed (He et al. 2007). Therefore pH plays a vital role in the synthesis of nanomaterials, by regulating the size, morphology and location of nanoparticles.

In a report by Juibari et al. (2011), an extremophilic bacterium, *Ureibacillus thermosphaericus* isolated from Ramsan geothermal hot springs located in Mazandatan province, Iran exhibited extracellular silver nanoparticle synthesize at higher temperatures (60–80 °C) under varying concentrations of $AgNO_3$ (0.001–0.1 M). Maximum nanoparticle synthesis was achieved at 0.01 M $AgNO_3$ at 80 °C. The biomolecules produced by the extremophile under extreme temperatures may play a major role in the synthesis of nanoparticles even under unfavorable temperature conditions. *Halomonas maura*, a salt tolerant bacterium produced mauran, a polysaccharide which plays a major role in synthesis of MR(muran)/CH(chitosan) nanoparticle, by polyelectrolyte complexation of CH and MR solution through strong magnetic stirring (Raveendran et al. 2015).

Another thermophilic bacterium, *Geobacillus stearothermophilus* was reported to synthesize nanoparticles of silver and gold nanoparticle. Gold nanoparticles synthesized by this extremophilic bacterium were spherical shaped and monodispersed with a size range of 5–8 nm. In case of silver nanoparticles, the particles were polydispersed, spherical shaped with a size range of 5–35 nm (Mohammed Fayaz et al. 2011). The authors stated that the free amine groups or cysteine residues present in the proteins were key components responsible for the synthesis of nanoparticles. They have also identified seven different proteins in the range of ascending 98 kDa-12 kDa that are bearing free amine or cysteine bearing molecules aiding nanoparticle synthesis. Similarly, gold nanoparticle synthesis by *Shewanella oneidensis* has been reported by Suresh et al. (2011). An extracellularly synthesized spherical gold nanoparticle particles of size 2–50 nm by *S. oneidensis* was found to be stable for several months. The particles were hypothesized to be synthesized by the reducing agents present in the cell membrane and were capped by the detachable protein or peptide coat. In 2012, Dhandapani et al. synthesized TiO_2 (Titanium oxide) nanoparticles using *Bacillus subtilis* which was reported to destroy biofilm forming microbes. In another study, 11 marine bacteria were screened for the synthesis of gold nanoparticle (Sharma et al. 2012). Among those strains, *Marinobacter pelagius* isolated from solar saltern in Kakinada (India), produced monodispersed gold nanoparticle of size 10 nm that were highly stable. This is one of the initial reports on the synthesis of gold nanoparticle by marine bacteria. They confirmed the role of extracellular biomolecules produced by the bacteria in reducing and capping of nanoparticles. A study by Dehnad et al. (2015) demonstrated gold nanoparticle synthesis by *Arthrobacter nitroguajacolicus*, isolated from Andaliyan gold mine in north-west of Iran. It exhibited intracellular synthesis of spherical shaped nanoparticles of about 40 nm in 24 h. However, not all bacteria are found to be capable of gold nanoparticle synthesis in shorter time periods. An alkalothermophilic actinobacterium, *Thermomonospora* sp. synthesized gold nanoparticle extracellularly taking 120 h for reduction of aurum ion. In the case of strains *Rhodococcus*, it reduced the aurum ion in 24 h, but the particles were synthesized intracellularly which complicated the extraction and also destroys the bacterial cells (Kalabegishvili et al. 2012).

MnO_2 nanoparticles were synthesized by the marine bacteria *Saccharophagus degradans* (Sde 2–40) using $KMnO_4$ as the substrate. Salunke and his colleagues (2015) ruled out the possibility of negative outcome on nanoparticle synthesis under the presence of several media components used for microbial growth. Recently, Srivastava et al. 2013 reported the synthesis of Tellurium nanoparticles (TeNPs) by haloarchea on *Halococcus salifodinae* BK3, which was isolated from the salt pan. The enzyme responsible for the synthesis of TeNPs was identified as tellurite reductase. The archea *H. salifodinae* was orange-red pigmented and the pigmentation was found to decrease with increased concentration of tellurite which turned the organism black against being orange-red. TEM analysis exhibited hexagonal needle-shaped nanoparticle with an average diameter of 10 nm and length of 44 nm. In *E. coli*, α-NADPH dependent sulfite reductase was extracted and used for the synthesis of gold nanoparticle. The particles were spherical in shape with 10 nm in size which was found to act as an antifungal agent (Gholami-Shabani et al. 2015).

Silver nanoparticle synthesis by psychrotolerant bacteria, *Pseudomonas mandelii* was reported by Mageswari et al. (2015). Its stability under long-term storage, and larvicidal activity under low-temperature conditions were investigated. Electron and atomic force microscopy studies revealed that 6 among 22 psychrotolerant isolates synthesized silver nanoparticles with an average diameter of 1.9–14.1 nm. *Pseudomonas mandelii* SR1 synthesized the least-sized silver nanoparticles with an average diameter of 1.9–10 nm, at temperatures as low as 12 °C without aggregate formation, and the synthesized nanoparticles were stable for up to 19 months of storage period. In larvicidal studies, LC90 (lethal concentration) values against *Anopheles subpictus* and *Culex tritaeniorhynchus* larvae were at 31.7 and 35.6 mg/L, respectively. The synthesis of nanoparticles on different temperature, pH, incubation time and storage stability in dark and light conditions was studied. In UV spectroscopy scan, the synthesized silver nanoparticle showed a peak around 420 nm, which is a characteristic of the surface plasmon resonance of silver nanoparticles. XRD analysis revealed the diffraction peaks at 46°, 54°, 68°, 26° and 32° corresponding to (2 1 1), (2 2 0), (2 2 2), (1 1 0) and (1 1 1) that were planes of silver and silver oxide. EDAX spectrum confirmed the presence of silver atom. In FTIR analysis, the presence of primary/secondary amines and sugar derivatives were confirmed. These results revealed that the protein and sugar molecules were responsible for the synthesis of silver nanoparticle. Further, the sugar derivatives were analyzed by HPLC. The synthesized silver nanoparticles showed larvicidal activity at low temperature which is non-toxic to environment.

Nanoparticle synthesis by psychrotolerant bacterium, *M. psychrotolerans* (Parikh et al. 2011) was investigated at temperatures as low as 12 °C and it showed enhanced synthesis at 22 °C reflect the cold-adapted physiology of the strain. Extracellular synthesis of silver nanoparticles using psychrophilic bacteria was investigated by Shivaji et al. 2011. The synthesized silver nanoparticles were characterized using

UV–Visible spectroscopy, transmission electron microscopy and atomic force microscopy. The sizes of the silver nanoparticles ranged from 6 to 13 nm and were stable for 8 months in the dark. The synthesis and stability of silver nanoparticles appears to depend on the temperature, pH or the species of bacteria (*P. antarctica* or *A. kerguelensis*) from which the supernatant is used. It was observed that the *A. kerguelensis* supernatant could not produce silver nanoparticles at the temperature where the *P. antarctica* could synthesize silver nanoparticles. This study provides evidence that the factors in the cell-free culture supernatants that facilitate synthesis of silver nanoparticles vary from bacterial species to species.

2.2.5.3 Fungi Mediated Synthesis of Nanoparticles

In recent years, there has been an increase in research focusing on the use of fungi for the synthesis of different types of nanoparticles (Dhillon et al. 2012). Research on fungi has been found to be preferred as they offer several advantages. One such benefit is that they could secrete large quantities of enzymes. Other benefit includes ease of handling compared to other microorganisms, which make the biosynthesis of nanoparticles using fungi potentially exciting (Table 2.7). However, one major concern is the genetic manipulation of some specific enzymes for over expression is much more difficult than in prokaryotes.

Fusarium oxysporum, is a fungus that has been often used for the biosynthesis of nanoparticles. *F. oxysporum* synthesizes extracellular gold nanoparticles which are spherical or triangular in shape and are at a size of 20–40 nm and they are found to be well dispersed with no significant reunion was found even after a month (Mukherjee et al. 2002). In another report, stable cadmium sulfide nanoparticles of size range 5–20 nm was synthesized by *F. oxysporum*. This nano-CdS was produced with the help of enzyme sulfate reductase when exposed to $CdSO_4$ solution. Similarly ZnS, PbS and MoS_2 nanoparticles also could be synthesized by *F. oxysporum* when incubated with corresponding sulfate (Ahmad et al. 2002). They also used *F. oxysporum* for biosynthesis of cruciform-shaped $CaCO_3$ crystals by exposing to aqueous calcium ions. In both of these studies the basic mechanism behind the synthesis is discussed as the role of enzymes present in fungi which played a crucial role during the synthesis (Rautaray et al. 2003).

Acidophilic fungus *Verticillium* sp. has been reported to produce intracellular silver nanoparticles in cytoplasm (Sastry et al. 2003). When *F. oxysporum* was utilized to synthesize alloy nanoparticles, surprisingly Au-Ag alloy nanoparticles were obtained which was the first reported on the fungus-mediated biosynthesis of Au-Ag alloy nanoparticles. The highly stable alloy nanoparticles in the size range of 8–14 nm were formed when the fungi were exposed to equimolar concentrations of $AgNO_3$ and $HAuCl_4$. The fungi *F. oxysporum* was demonstrated to secrete NADH-dependent enzymes and it was confirmed that the nano-alloy composition was different in the control of the amount of NADH (Senapati et al. 2005). In 2006, it was reported that the substantial amorphous hydrated silica in the rice husk could be bioleached and biotransformed into quasi-spherical crystalline silica nanoparticles

Table 2.7 Fungi-mediated nanoparticle synthesis

Fungi	Type of nanoparticle	Morphology	Size range (nm)	Location/ organelle	References
Fusarium oxysporum	Gold	Spherical or triangular	20–40	Extracellular	Mukherjee et al. (2002)
F. oxysporum	Cadmium sulfide , Zinc sulfide, Lead sulfide and Molybdenum disulfide	Hexagonal (CdS)	5–20	Extracellular	Ahmad et al. (2002)
Verticillium sp.	Silver	–	2–20	Cytoplasm, Intracellular	Sastry et al. (2003)
F. oxysporum	Au-Ag alloy	Spherical	8–14	Extracellular	Senapati et al. (2005)
Aspergillus flavus	Silver	Isotropic	8.9	Surface of cellwall	Vigneshwaran et al. (2007)
F. oxysporum	Lead sulfide	Spherical	5–30	Extracellular	Syed and Ahmad (2012)
F. oxysporum	Zinc sulfide	Spherical	42	Extracellular	Mirzadeh et al. (2013)
F. semitectum	Silver	Spherical	10–60	Extracellular	Basavaraja et al. (2008)
V. luteoalbum	Gold	pH3 spherical, pH5- spherical, triangular, hexagons, spheres and rod, pH7,9- small spherical, and irregular shaped particles	10–100	Intracellular	Gericke and Pinches (2006)
Agaricus bisporus	Silver	Spherical	8–20	Extracellular	El-Sonbaty (2013)
Botrytis cinerea	Gold	Spherical, pyramidal, hexagonal, triangular and decahedral	1–100	Extracellular	Castro et al. (2014)

in a size range of 2–6 nm. Further studies demonstrated that the amorphous hydrated silica could be bioleached by the proteins secreted by the cells. However, amorphous hydrated silica could not be biotransformed into silica nanocrystallites by these proteins alone (Bansal et al. 2006). The fungi *Aspergillus flavus* has been reported to synthesize silver nanoparticles on the surface of cell wall with size ranging in 8–9 nm. Proteins present on the cell wall were hypothesized to be responsible for the reduction and stability of the particle (Vigneshwaran et al. 2007).

Extracellular platinum nanoparticles with the size ranged 5–30 nm were obtained when the *F. oxysporum* incubated with H_2PtCl_6 which were stabilized by proteins (Syed and Ahmad 2012). Biosynthesis of spherical ZnS nanoparticles with the average size of 42 nm was also reported using *F. oxysporum* (Mirzadeh et al. 2013). It was found that other species of *Fusarium* such as *F. acuminatum* (Ingle et al. 2008) and *F. semitectum* (Basavaraja et al. 2008)could also be used to synthesize extracellular silver nanoparticles with size of 10–60 nm with spherical in shape. The synthesized particles were stable for weeks. In fungus *V. luteoalbum*, gold nanoparticle synthesis was found to occur at different conditions of pH. At pH 3, spherical shaped particles were formed. However at pH 5 with spherical, triangular, hexagons, spheres and rod shaped particles were observed and when the pH was increased to 7 and 9, small spherical and irregular shaped particles were formed (Gericke and Pinches 2006).

Silver nanoparticles synthesis has also been reported when aqueous extracts of *Agaricus bisporus* were used. A study using *Agaricus bisporus* revealed that these nanoparticles were of spherical shape and size ranging between 8 and 20 nm (El-Sonbaty). Biosynthesis of gold nanoparticles by fungus *Botrytis cinerea* was reported first in 2014. This gold nanoparticle synthesis was found to result in nanoparticles of various shapes such as spherical, pyramidal, hexagonal, triangular and decahedral of sizes ranging between 1 and 100 nm. Biomolecules secreted by the fungus were responsible for the production of gold nanoparticles, but the exact mechanism remains to be elucidated (Castro et al. 2014).

2.2.5.4 Yeast in Synthesis of Nanoparticle

Studies on biosynthesis of metallic nanoparticles by yeast are few compared to bacteria and fungi (Table 2.8). Available research carried out on yeast mostly deal with the synthesis of quantum semiconductor nanocrystallites. Extremophilic yeasts isolated from the drainage of acid mine have been utilized for the synthesis of Ag and Au nanoparticles. Yeasts are reported to exhibit growth up to concentrations such as 1.5 mM Ag ion and 0.09 mM Au ion and nanoparticle synthesis is mainly extracellular in nature with the produced particles around 20–100 nm in size synthesized (Mourato et al. 2011). The most commonly studied yeast *Sachharomyces cerevisae* has also been used in the biosynthesis of metallic nanoparticles in recent years. Biosynthesis of TiO2 nanoparticles using the *S. cerevisae* yielded in nanoparticles of size 8–35 nm and it was proposed that the quinones and membrane bound oxidoreductases might affect the formation of TiO2 nanoparticles (Jha et al. 2009). The yeast *S. cerevisae* was investigated for the synthesis of MnO_2 nanoparticle in both extra and intracellular manner. All experiments showed positive result with spherical and hexagonal shaped nanoparticle ranging 30 nm in diameter (Salunke et al. 2015). Report also exists on gold nanoparticle synthesis using the yeast *S. cerevisae*

Table 2.8 Yeast-mediated nanoparticle synthesis

Yeast	Type of nanoparticle	Morphology	Size range (nm)	Location/ organelle	References
Extremophilic yeast	Ag and Au	Spherical	Silver nanoparticle- 20, Goldnanoparticle- 30–100	Silver nanoparticle- extracellular	Mourato et al. (2011)
Sachharomyces cerevisae	Titanium Oxide	Spherical	8–35	Extracellular	Jha et al. (2009)
Yarrowia lipolytica	Gold	Hexagonal and triangular shaped at pH 2, 7 and 9	15	cell wall	Agnihotri et al. (2009)
S. cerevisae	Manganese oxide	spherical and hexagonal	30	Intra and extracellular	Salunke et al. (2015)

(Lin et al. 2005). When gold nanoparticles synthesis was studied in *Yarrowia lipolytica*, the particles were associated with the cell wall and were hexagonal or triangular in shape at varying pH of 2, 7 and 9. Reductases were reported to have a major responsibility in nanoparticle production by yeasts. A method to extract cell wall associated nanoparticles from yeasts using a freeze and thaw method was proposed (Agnihotri et al. 2009).

2.2.5.5 Actinomycetes in Synthesis of Nanoparticle

Actinomycetes are widely distributed in nature and have the characteristics of both fungi and bacteria. Gold nanoparticles have been reported to be synthesized successfully with *Rhodococcus* sp. When an alkalotolerant actinomycete was used for intracellular synthesis of gold nanoparticle particles with the dimension of 5–15 nm were produced (Ahmad et al. 2003). This was the very first report on the extracellular synthesis of gold nanoparticle with the use of bacteria. These thermoactinomycetes are able to restore gold ion into spherical NPs with good monodisperity at an average size of 8 nm. The FTIR analysis demonstrates that the surface of the gold nanoparticle was amide (N) and (O) protein, which are stable factors that promote these Nanoparticles.

A recent report demonstrates gold nanoparticle production by *Streptomyces viridogens* strain [HM10] a novel actinomyces. The strain was reported to follow an intracellular mechanism for synthesis of gold nanoparticles. Electron microscopy (TEM) study on the strain revealed the presence of spherical and rod shaped gold mycelium and X- ray diffraction analysis demonstrated that their average size to be 18–20 nm. At the same time, the strain HM10 showed increased growth at 1 and 10 mM concentration of $HAuC1_4$. In addition the gold nanoparticles produced by the strain HM10 possessed high antibacterial activity against *S. aureus* and *E. coli*

(Balagurunathan et al. 2011). Nanoparticle production by *S. albidoflavus* has been found to be both extracellular and intracellular. An interesting phenomenon observed was that that the nanoparticles synthesized by this strain were reaction-time dependent. The average size of these nanoparticles from *S. albidoflavus* was found to be 14.5 nm. By varying pH and reaction time multidimensional gold nanoparticles were generated (Prakasham et al. 2012). Thirty five marine actinobacterial strains were isolated from marine sediment of Busan coast, South Korea and employed for the biosynthesis of gold nanoparticle. In that, *Nocardiopsis* sp. MBRC-48 exhibited the production of extracellular gold nanoparticles. The synthesized nanoparticles have been characterized using UV-visible spectral analysis, XRD and FTIR. In FTIR analysis, the results clearly evidenced that the nanoparticle formation occurred by proteins, enzymes and metabolites. EDAX spectroscopy revealed that the presence of elemental gold peak. TEM analysis confirmed that the particle were spherical in shape and non-uniformly distributed with size ranges from 7 to 15 nm and they evaluated the antibacterial, antioxidant and cytotoxicity of the nanoparticles (Manivasagan et al. 2015). Few reports for Actinomycetes-mediated synthesis of nanoparticles list in the Table 2.9.

2.2.6 *Characterization of Nanomaterials*

Several sophisticated techniques being continuously developed for characterization of the size, shape, stability, of nanomaterial as well as to determine and identify the presence of metal signals in the synthesized nanomaterials (Table 2.10). Characterization of nanomaterials can be carried out using two major strategies which are spectroscopy and microscopy techniques.

Table 2.9 Actinomycetes-mediated synthesis of nanoparticles

Actinomycetes	Type of nanoparticle	Morphology	Size range (nm)	Location/ organelle	References
Alkalotolerant actinomycete (*Rhodococcus* sp.)	Gold	Spherical	5–15	Intracellular	Ahmad et al. (2003)
Streptomyces viridogens strain [HM10]	Gold	Spherical and rod shaped	18–20.	intracellular	Balagurunathan et al. (2011)
S. albidoflavus	Silver	Spherical	14.5	extracellular and intracellular	Prakasham et al. (2012)
Nocardiopsis sp.	Gold	Spherical	7–15	extracellular	Manivasagan et al. (2015)

Table 2.10 An overview of techniques to characterize physio-chemical properties of nanomaterials

Spectroscopy Techniques	Instruments	Mass	Number	Size Distribution	Shape	Aggregation state	Surface area and charge	Chemical composition
	UV-vis Spectroscopy			✓				✓
	X-ray Diffraction			✓				✓
	FT-IR Spectroscopy							✓
	Raman Spectroscopy							✓
	Atomic Absorption/ optical emission spectroscopy							✓
	Mass spectroscopy	✓						✓
	X-ray photoelectron spectroscopy							✓
	Dynamic light Scattering			✓		✓		
	Zeta potential						✓	
Microscopy techniques	Scanning electron microscopy		✓	✓	✓	✓		
	Transmission electron microscopy		✓	✓	✓	✓		
	Scanning probe microscopy		✓	✓	✓	✓		

2.2.6.1 Spectroscopic Techniques

Ultraviolet-Visible Spectroscopy

Nanoparticles from metals such as gold and silver interact strongly at specific wavelengths of light (500–600 and 400–450 nm) based on their optical property and surface plasma resonance.

Such characteristics of the nanoparticles can be attributed to free flow electron oscillation in the elements composing the nanoparticles being induced by the electromagnetic field (Noruzi et al. 2011). However, these techniques are used only to detect metallic nanoparticles and are often not compatible with other nanomaterials. A change in color of the initial solution to red or violet for gold nanoparticles indicates the presence of synthesized nanomaterials in the extract and the solution turns brown in case of silver nanoparticles (Noruzi et al. 2012). Thus color change indicates and influences the absorption pattern which confirms the presence of synthesized nanomaterials in the extract. The plasma resonance property has been found to vary with size and shape of nanoparticles. A change in surface resonance due to variation in particle size may lead to a shift in wavelength from red (increase in particle size) and blue (reduction in particle size). However, in several cases adverse effect in the position of plasma resonance has been observed due to factors such as environment dielectric properties, interactions that are physical or chemical which happens on the particle surface, surface charge, interparticle distance as well as aggregation. Asymmetrical and broad plasma resonance bands indicate that diverse orientation of material often results in formation of anisotropic nanoparticles (Kasthuri et al. 2009; Noruzi et al. 2011).

X-Ray Diffraction

XRD is one of the most powerful techniques to study the structure of nanomaterial which provides us data regarding the width and shape of the nanomaterials (size of crystalline, lattice, dislodgment of particle structures, etc). Samples are often prepared as smear or compact flat or in capillary and are exposed to a monochromatic beam of X-ray which is diffracted by the nanomaterial and data on the diffracted beam is collected at an angle (2θ) with respect to the incident beam. A powder diffraction pattern supplies information from the nanomaterial on phases present, phase concentrations, structure, as well as the degree of crystallinity or amorphous content followed by details on crystallite size/strain. The peak widths in given phase pattern provides information on the average crystallite size where large crystallites give rise to sharp peaks and any increase in the peak width indicates a reduced crystallite size.

The measure of the crystallite size does not equal to the size of the particle as a single nanoparticle can be an aggregate of several crystallites. Peak broadening also occurs as a result of variation in d-spacing caused by microstrain. The average crystallite size can be determined from the breadth of the peaks in an X-ray diffractogram, assuming no lattice strain or defects are observed, through the Debye-Scherrer equation (Dubey et al. 2010). Comparison of average particle sizes either using a power XRD or TEM methods can help us obtain the crystal structures of nanoparticles. An important parameter to be considered is X-ray coherence length, which gives us an approximation of the average size of crystalline domain of nanomaterial (XRD-size), whereas total size of the particles (TEM-size) can be viewed from the TEM metaphors (Schmid 2004). A major disadvantage of using these techniques is that it is very difficult to find out the single conformation and binding state of growing crystals followed by occurrence of low intensity diffracted X-rays in low atomic number materials (Cao 2004). A recent study has proposed the use of a femtosecond pulse to determine the macromolecules for non-matured crystal (Chapman et al. 2011).

Fourier Transformed Infrared Spectroscopy

FT-IR is primarily used to determine the functional groups of the protein bound over the surface of nanomaterials or functional groups of exoploysaccharides which act as capping agents and thereby improve stability during biological synthesis of nanomaterials. Identifying such biomolecules is important to change or enhance the chemical structural composition which may leads to understand the development of their properties and probable future applications. These types of biomolecules in biological suspension falls into absorption spectrum in the range of 1000–1800 cm^{-1} (C=C, C=O, C-N, C-O) which indicate the possible role of those compounds in maintaining the nanoparticle stability. The stretching peak for amine and amide groups during an FT-IR analysis falls in the range between 3200 and 3500 cm^{-1} (N-H and O-H) (Philip 2010).

Dynamic Light Scattering

DLS technique is used to study the size distribution and hydrodynamic average particle size of nanoparticles. The basic principle behind this technique is that the movement of a particle depends on time of fluctuation in light scattering to the suspension which is based on Doppler effect (Brar and Verma 2011). Determination of particle size distribution is not completely known due to adverse effect on particle suspension, scattering angle and shape of nanoparticles. This technique is especially important in reuse of nanoparticles, as the samples can be used for other characterization. In addition, scattering of light is directly proportional to sixth power of particle radius; this reason helps extremely to determine the presence of small aggregates. This technique is quicker and less expensive than that of microscopy technique for analysis the size of nanomaterials (Bankar et al. 2010).

Zeta Potential

Zeta potential is an instrument to measure the electrostatic potential of nanomaterial by supplying electric field between dispersion medium and stationary layer of fluid. Zeta potential difference of nanomaterials between -10 to +10 mV are considered as neutral, whereas greater than +30 or less than -30 mV are considered as cationic or anionic charged particles. Almost all biologically synthesized nanomaterials were strongly cationic charged particles due to negatively charged cell membrane which displaying more toxic associated with cell wall disruption (Clogston and Patri 2011). Dilution of concentrated samples which does not affects the results of synthesized nanoparticles it may due to shift in zeta-potential value was attributed to an increase in contribution of the signal from extraneous particulate matter (Tantra et al. 2010). Zeta potential and hydrodynamic size can be altered by charging the pH of the solution. At low pH, nanomaterial have a positive surface and inversely, at high pH, a negative surface charge. The isoelectric focusing point is intermediate pH it results in net charge of particles will be zero. State and stability of nanoparticles depends on pH, surface charge and coating surface. From profound studies, pH can change the dispersion state by altering the zeta potential which influences the ionic strength of dispersion medium by altering the double layered surface electric charge of nanomaterial (Jiang et al. 2009).

Other Spectroscopy Techniques

To characterize the physio-chemical properties of nanomaterials, other techniques like X-ray photoelectron spectroscopy (XPS), Inductively coupled plasma atomic emission spectroscopy (ICP/AES), Raman scattering (RS), Fluorescence correlation spectroscopy (FCS), circular dichroism (CD), Mass Spectroscpy (MS) were used.

2.2.6.2 Microscopy Techniques

Transmission Electron Microscopy

The transmission electron microscope (TEM) is the most very powerful tool for probing the structure of nanosized particles. It is not only can give morphological information of shape and size of material even able to define at atom level of the nanomaterials. To analyse the structure of nanomaterials by two types of mode either Bright-field TEM of Dark field TEM. In Bright-field TEM, is most common type of mode to imaging the nanomaterials in which images are captured by direct exposure of transmitted electrons and any type of materials can be visualized in the form of liquid or solid. In dark-field TEM, directly use diffracted electron at specific set of crystal plane. Mainly, it is used to locate defect in the crystal. For imaging the nanomaterials using TEM depends on their contrast of sample relative to the background. Samples are prepared for imaging by drying nanoparticles on a copper grid that is coated with a thin layer of carbon. Materials with high electron densities can able visible directly than amorphous carbon such as metals (silver, gold, copper, aluminium) and most of the oxides and other materials as to be coats with tungsten-gold materials. Size and morphological distribution of nanomaterials is straight forward if it is individual non-aggregated samples. Otherwise, it is statistically difficult to image the particular size and shape of the nanomaterial. Since the presence of polymeric structure (irregular or more than one size) of nanomaterials in dispersion, the resulting statistical representation in average and standard deviation of the sample may not be accurate. For irregular shape nanomaterials an alternative method is used to image by cross sectional area or convert the area to an equivalent spherical diameter by using softwares.

The fast electrons used in a TEM are capable of penetrating many atomic planes and so are diffracted by crystalline regions of material just like X-rays. Their wavelength (~ 0.04 nm for Eo ~ 100 keV) is much less than a typical atomic-plane spacing (~ 0.3 nm) so that according to the Bragg equation $n\lambda = 2d\sin\theta$, Bragg angles θ are small. In addition the integer n is usually taken as unity, since nth order diffraction from planes of spacing d can be regarded as first order diffraction from planes of spacing d/n (Wittstock 2001). Diffraction represents elastic scattering of electrons in a crystal. The regularity of the spacing of these nuclei results in a redistribution of the angular distribution of the scattered intensity. Instead of continuous distribution over scattering angle, there are sharp peaks centered on certain scattering angles, each twice the corresponding Bragg angle θ. In the TEM this angular distribution can be displayed by magnifying the diffraction pattern first formed at the back focal plane of the objective lens. Examination of the TEM image of the polycrystalline specimen shows that there is a variation of electron intensity within each crystallite. This diffraction contrast arises either from atomic defects within the crystal or the crystalline nature of the material itself, combined with the wave nature of transmitted electrons.

The resolution of the TEM could be improved by special arrangements of the magnetic fields serving as focuses of the electron beam, by enhancing the energy of the electrons. The main advantages of the HRTEM are the direct observations of the detailed nanostructures, such as the core/shell structure, the interfaces and the surfaces, the atomic defects (including point defects, dislocation, planar defects) the twin structures etc (West 2007). The nanocrystal characterization can be done using transmission microscopy. Here, an electron beam is used to image a thin sample in transmission mode. The resolution is a sensitive function of the beam voltage and electron optics: a low-resolution microscope operating at 100 kV might have a 2–3 Å resolution while a high voltage machine designed for imaging can have a resolution approaching 1 Å.

Three main issues are causing major problems during image process such as particle agglomeration, Impurities in the samples and few particles in images.

Particle Agglomeration A number of factors influences how sample synthesized and preparation conditions namely, dynamic property of dispersion or diffusion of particles in the solvent during drying and concentrating process.

Impurities in the Sample Due to electron density present in the sample and in the dispersion. i.e., presence of salt, silica, etc.

Few Particles in Image It's mainly due to the way of sample preparation, in that presence of low or dense particles in the gird.

Recently, Scanning Transmission Electron Microscope (STEM) has advanced to generate images by staging a scan of a narrow electron beam over the samples and coupled with high-angle annular dark-field (HAADF) detector. Other detectors such as Energy-dispersive X-ray spectroscopy (EDX) and Electron energy loss spectroscopy (EELS) used for analysis elements by qualitative and quantitatively. In addition, cryo-TEM an equipment to examine biological samples under cryogenic temperature, preventing them from structural deformation caused by electron beams and by the conventional sample treatment during ultra-sectioning.

Scanning Electron Microscopy

Scanning electron microscope (SEM), which is used to observe the morphology of a surface of sample and back scattering of electrons at higher magnification, higher resolution and depth of focus. SEM creates a low-energy beam of electrons (1–30 keV) and detecting the electrons scattered off the sample. Samples for SEM are mounted on aluminum or carbon stubs either in the liquid or solid form. Unlike TEM, in SEM, prepared samples can be introduced for imaging in bulk form, as there is no need to cut thin sections. Generally, sample preparation is less tedious for SEM imaging, compared to TEM. For example, liquid samples can be dried directly on the SEM stub (Lorenz et al. 2010), or closed in agar capsules that, after chemical treatment, undergo notch (Egelandsdal et al. 1999). In addition, Focused-ion beam scanning electron microscope (FIB-SEM) the ion beam can cut into the material and a solid specimen can be sectioned for 3D imaging and also gives the possibility of tilting the sample to allow observation from different angles and 3D imaging. A camera is used to photograph the image or it may be digitized and processed on a computer. The characteristic X-rays emitted may be analyzed for their energy and intensity (EDX), the energy being the signature of the element emitting them and the intensity as to how much of it is present. SEM while having lower resolution than TEM, is able to image nanoparticles on bulk surfaces and for direct visualization of nanocrystals in larger assemblies (Khler and Fritzsche 2004).

Scanning Probe Microscopy

Most advance equipment to determine the surface structures are the atomic force microscope (AFM) and scanning tunneling microscope (STM). These techniques are capable of imaging the local surface topography with atomic resolution (Wiesendanger 1994).

Atomic Force Microscopy

Atomic force microscope (AFM) and scanning force microscope (SFM) are the most common techniques from the SPM family and play a major role in research and development part of nanotechnology. Both these methods are based on minute but measurable forces between a sharp metallic tip and atoms present on a surface. Atomic force microscope (AFM) was invented by Gerd Binning in the year 1986. The tip is usually mounted on arm called cantilever which is flexible in nature, and the entire set up is placed at subnanometer distance from the sample surface. As the tip is brought closer to a sample placed on the surface, interatomic forces between the tip and the atoms in the samples causes the cantilever to curve finely which is detected optically by a laser beam reflecting off from the back of the cantilever. When the tip scans over the entire sample surface, an image which is proportional to the deflections of the cantilever can be obtained, which basically represents the three dimensional structure of the sample surface. When the tip is made to scan the sample in the X-Y plane, it senses the attractive or repulsive forces arising from the surface atoms which are then redirected to the Z direction (Sarid 1991). Primarily, there are two ways in which atomic force microscopy can be applied namely contact mode and non-contact/tapping mode. During the contact mode, the tip is placed within few angstroms from the sample surface, and there are direct interactions occurring between the atoms on the tip and on the sample surface. It is highly complex to describe the atomic force interactions occurring during the contact mode and requires molecular dynamics stimulation of the coulombic interactions taking place between charges or charge distribution, followed by polarization caused due to induced dipole moments as well as quantum mechanical forces when the electrons in the orbital start to interact, for each pair of atoms residing on the tip and the sample surface. Despite its complexity, the contact mode is the usual choice to study by researchers to study surface morphology of particles with atomic resolution (Sarid and Coratger 1991). The distance between the tip and the sample is increased in the non-contact mode, usually between 2 and 30 nm. The non-contact mode describes the forces between the sample surface and tip in terms of macroscopic interactions. The tapping mode requires the sample to have a flat surface and a spherical tip. Other forces may such as electrostatic force and magnetostatic force may also play a role in influencing the interactions between sample surface and tip. The forces in the non-contact mode are on average of 2–4 orders smaller in magnitude than forces occurring in the contact mode. Details on the sub nanometer scale are not possible to obtain in the non-contact methods as the interactions that occur are only between larger portions of the tip and the sample. The non-contact mode is mainly used for study and capture magnetic domains or electronic devices. An atomic force microscope is primarily used to identify the sample's surface characteristics at the atomic level, including its topography as well as the magnetic and electrical properties. AFM creates a highly magnified 3D image of a surface which helps us to directly view surface features which may only have nanometer-sized dimensions including those such as single atoms and/or molecules on a surface. This gives researchers the facility to directly visualize objects that are of nanometers in size and measure various dimensions of the surface features (Binnig et al. 1982; Lang et al. 2002).

Scanning Tunneling Microscopy

Scanning tunneling microscope or STM, belonging to the SPM family was invented in 1982 by Gerd Binning and Heinrich Rohrer remains a key tool used in nanotechnology. STM is primarily used to study surface properties at an atomic level and works on the principle of measuring the tunneling current between a sharpened metallic tip and surface of a conducting material. When a small bias of voltage is applied between the atomically sharp tip and the sample, there is no flow of current if the distance separating the tip and the sample is large. On the contrary, current flows across the space when the tip is brought closer but without physical contact towards the sample. Such a current is termed as a tunneling current which is the consequence of overlapping wave functions occurring between the atom on the tip and opposite atom on the sample surface. When there is small bias voltage, the electrons are able to travel across a vacuum barrier from the tip and reach the sample. However, the degree of the tunneling current is extremely sensitive and relies on the distance that separates the tip from the sample, the local electron density in the sample as well as the local barrier height. STM is typically performed on conductive and semiconductive surfaces and the atomic information of the surface of the samples can be mapped out as well as the topography of surface electronic states measured. Some of the common applications of STM are atomic resolution imaging and electrochemical STM whereas scanning tunneling spectroscopy (STS) aids imaging of poorly conductive samples (Ong et al. 2013).

2.2.7 Conclusion

As an innovative branch among emerging sciences nanotechnology has the potential to completely revolutionize our lives. There exists a massive variety of nanomaterials today which posses a wide range of properties with the potential to be developed into endless applications. Despite its description as an emerging technology, several indications exist that are examples of human use of nanomaterials for centuries such as the ruby colour in crystals which are caused by gold nanoparticles that are trapped within the crystal matrix. Emerging studies describing the manipulation of materials at their atomic level has paved way for the development of nanomaterials ranging in the sizes scaling 1–100 nanometres. Modification of material properties on a molecular scale offers the prospective for upgrading performance for applications in every aspect of human activity. The potential applications for nanomaterials in the future are limitless, with chances of producing significant advances in the fields of electronics, food, medicine, computing, etc.

Thus the use of nanomaterials can hope to bring a range of benefits to society. On the economical front, science and technology are key participants in improving the economy and life quality, both of which are proposed to be improved by commercialization of positive nanomaterial technologies. In terms of energy efficiency, nanomaterials can have a huge impact as it is proposed that they are functional even at higher temperatures and hence can improve efficiency of power plants, thereby enabling the development of new energy generation systems. However, industrial-scale production of nanomaterials could be possible only when they provide performances similar to conventional materials at a much reduced cost and cause less environmental impacts compared to conventional materials. Thinking along similar lines, though its impact in the future and implications has debated over the last decade, products making use of nanomaterials and nanotechnology has gradually started to arrive. Keeping in mind several other technologies and innovations which faced initial reluctances and antagonism, nanotechnology follows the same path causing alarms in terms of its environmental impacts or the economy. Further, research related to production and applications of nanomaterials has gained significant improvements by receiving funding from both private and government categories in the recent years. Therefore until the benefits of nanomaterials are disproved, research on nanomaterials as well as nanotechnology must be encouraged.

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Chapter 3
Synthesis and Toxicity of Silver Nanoparticles

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Abstract Silver nanoparticles (AgNP) are used in many economic sectors, but they are potentially toxic for living organisms. Nanotoxicology studies of the toxicity of nanomaterials, which can be divided into those derived from combustion processes, manufacturing processes and naturally occurring processes. Insects are experimental models used to estimate the toxicity of nanoparticles. However, the mechanism of AgNP toxicity remains unclear. Here we review the synthesis, properties and toxicity of nanoparticles.

Keywords Insect • Silk worm • *Bombyx mori* • National nanotechnology initiative • Silver • Nanotoxicology • Larva • Pupa • Adult moth nanotoxicity

3.1 Introduction

Since many years, people have been preparing the glass windows with tiny colored metal particles, especially silver which provides glassy yellow colour (Solomon et al. 2007). The history of nanomaterials is quite long; nevertheless, major developments within nanoscience have taken place during the last two decades. The idea of Nanotechnology was first highlighted by Noble laureate Richard Feynman, in his famous lecture at the California Institute of Technology on 29th December, 1959. Richard Feynman in one of his articles published in 1960 titled, "There is plenty of room at the bottom" discussed the idea of nanomaterials. In 1970, Norio Taniguchi first defined the term Nanotechnology. According to him, "Nanotechnology mainly

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consists of the processing of, separation, deformation, and consolidation of material by one atom or by one molecule". And in 1980, another technologist, K. Eric Drexler promoted technological significance in nano scale.

Nanoparticles are being used in different fields including electrical, medical, biological, textile and chemistry in which the shape and size of colloidal metal particles play crucial role in different application including preparation of magnetic and electronic devices, wound healing, anti microbial gene expression and in the preparation of bio composites. Noble metal colloids have the optical and catalytically electromagnetic properties that dependent on the size and shape of the particles.

3.2 Silver Nanoparticles

Silver nanomaterials are fine particles of metallic silver that have at least one dimension less than 100 nm. Nano silver or suspensions of Nano silver refers to colloidal silver. To produce colloidal silver, a positive electrical current is applied through pure silver bars suspended in water, resulting in colloidal silver particles with the size range of 15–500 nm. Before the invention of penicillin in 1928, colloidal silver was used to treat many infections and illnesses. Unique properties of nano silver are mainly attributed to the high surface area to volume ratio, leading many industrial sectors to incorporate silver nanomaterial into their products. A variety of chemical and physical procedures could be used for synthesis of metallic nanoparticles.

The extraordinary optical properties of silver nanoparticles were used by glass founders as far back as in the time of the Roman Empire. This is evidenced by the so-called Lycurgus cup (fourth century AD) now exposed in the British Museum. A detailed study of the composition of its bronze-mounted insets of stained glass, carried out in the late twentieth century, revealed the presence of metal nanoparticles (with the average diameter of 40 nm) that is an alloy of silver (70 %) and gold (30 %) (Barber and Freestone 1990).

Silver is widely used as a catalyst for the oxidation of methanol to formaldehyde and ethylene to ethylene oxide (Nagy and Mestl 1999). Colloidal silver is of particular interest because of its distinctive properties, such as good conductivity, chemical stability, catalytic and antibacterial activity (Frattini et al. 2005). For example, silver colloids are useful substrates for surface enhanced spectroscopy, since it partly requires an electrically conducting surface (Tessier et al. 2000; Rosi and Mirkin 2005).

3.3 Properties of Silver Nanoparticles

The principle parameters of nanoparticles are their shape (including appropriate aspect ratios), size and morphological substructure of the substrate. Silver nanoparticles have diverse properties like catalysis, magnetic and optical polarizability, electrical conductivity, microbial activity and enhanced Raman scattering. They possess unique optical properties because they support surface plasmons. At specific wavelengths of light the surface plasmons are driven into resonance and the Silver nanoparticles have a distinct color that is a function of their size, shape and environment (Noguez 2007). The Plasmon resonance of Silver nanoparticles is responsible for the yellow colour in solution. Any visible change to the nanoparticles in solution typically indicates the aggregation of the nanoparticles (Pietrobon and Kitaev 2008). Silver nanoparticles are extraordinarily efficient in absorbing and scattering light. Many dyes and pigments have a color that depends upon the size and shape of the particles. An unique property of spherical Silver nanoparticles is Surface Plasmon Resonance peak wavelength that can be tuned from 400 nm (violet length) to 530 nm (green length) by changing the particle size and the local refractive index near the particle (Shipway et al. 2000).

3.4 Synthesis of Silver Nanoparticles

Optoelectronic, physicochemical and electronic properties of metal nanoparticles are determined by their size, shape and crystallinity. Therefore, the synthesis of monodispersed nanoparticles with different sizes and shapes remains a challenge. Metal nanoparticles are particularly interesting nanoscale system because of the ease in its synthesis and chemical modifications. Hazardous substances such as sodium borohydride, tetrakish hydroxyl methyl phosphonium chloride (THPC), poly-N-vinyl pyrrolidone (PVP) (Han et al. 1999; Esumi et al. 2001) and hydroxylamine were used for the synthesis of nanoparticles in the traditional wet methods. Other dry methods such as UV irradiation, aerosol and lithography (Tolles 1996) are not considered environment-friendly.

There are three major processes involved in the synthesis of nanoparticles. They are physical, chemical and biological method. The biological synthesis of metal nanoparticles (especially gold and silver nanoparticles) using plants (inactivated plant tissue, plant extracts and living plant) has received more attention as a suitable alternative to chemical and physical methods. Synthesis of metal nanoparticles using plant extracts is very cost-effective, and therefore can be used as an economic and valuable alternative for the large-scale production of metal nanoparticles. Extracts from plants may act both as reducing and capping agents in the synthesis of nanoparticles. The bio-reduction of metal nanoparticles by the combinations of biomolecules found in plant extracts is environmentally benign (Thakkar et al. 2010).

Several plants are utilized in the field of nanotechnology, to synthesize nanoparticles. Both silver and gold nanoparticles are synthesized using plants because of its easy availability and medicinal value. Even though many of the plant extracts have anti-cancerous and anti microbial activity, the plant derived nanoparticles shows enhanced activity because of the size. They also have their application in the agricultural pest control in which many of the plants have potential larvicidal activity.

Aqueous extracts of *Eclipta prostate*, lotus (*Nelumbo nucifera*) derived from silver nanoparticles showed potential larvicidal activity against *Sitophilus oryzae* (Abduz et al. 2012), *Anopheles subpictus* and *Culex quinquefasciatus*, respectively.

Plants such as *Eucalyptus* hybrid (Dubey et al. 2010), *Pelargonium graveolens* (Shankar et al. 2003a), Xerophytes Bryophyllum, Mesophyte *Cyperus* sp, Hydrophyte *Hydrilla* sp, Neem (Shankar et al. 2004a), *Aloe vera* (Chandran et al. 2006), *Hevea brasiliensis* (Bakar et al. 2007), *Cinnamomum camphora* (Huang et al. 2007), *Carica papaya* (Namrata et al. 2009), *Sesuvium portulacastrum* (Nabikhan et al. 2010), *Magnifera indica* (Philip 2011)*, Ocimum sanctum* (Krishna tulsi) (Philip and Unni 2011) and many other plants are utilized in the field of nanotechnology for synthesis of nanoparticles in various applications. Bankar et al. (2010) synthesized nanoparticles from banana peel extract which showed antifungal activity against *C. albicans, C. lypolytica* and anti bacterial activity against *C. koseri, Pesudomonas aerogenes, E. coli, P. vulgaris.* Autoclaved gum kondagogu (*Cochlosperum gossypium*) was also reported to have strong antibacterial activity. *Curcuma longa* powder was immobilized in cotton cloth and it is utilized in the synthesis of nanoparticles. Lemon juice and tansy fruit juice are also reported as potential reducing agents in the synthesis of silver nanoparticle. Nanoparticles synthesized from *Coriandum sativum* have commercial application in the optical limiting. Weeds are the unwanted plants in the agricultural field, But they are used in the synthesis of nanoparticle. Weeds such as Parthenium (Parashar et al. 2009), *Ipomoea aquatica, Enhydra fluctuans* and *Ludwigia adscendens* (Roy and Barik 2010) also have the capacity to reduce complex silver to nanoform.

Material Scientists are conducting research to develop novel materials with better properties, more functionality and lower cost than the existing ones. Several physical, chemical and biological synthesis methods have been developed to enhance the performance of nanoparticles with the aim to have a better control over the particle size, distribution and morphology (Shankar et al. 2003a, b). Synthesis of nanoparticles to have a better control over particles size, distribution, morphology, purity, quantity and quality, by employing environment friendly economical processes has always been a challenge for the researchers.

3.4.1 Physical Method

Several methods including the commonly used attrition and pyrolysis can be used for physical synthesis of metallic nanoparticles. In addition, macroscale or microscale particles are ground by a size-reducing mechanism. The production rate of these aforementioned "physical" procedures for achieving synthesis of metallic nanoparticles is quite low and, importantly, the expense is very high. Disadvantage of physical method the enormous consumption of energy to maintain the high pressure and temperature that is used in the synthesis procedures. In contrast, most of the bioprocesses occur under normal air pressure and temperature, resulting in vast energy savings (Thakkar et al. 2010).

3.4.2 Chemical Method

Chemical reduction is the most frequently applied method for the preparation of silver nanoparticles as a stable, colloidal dispersions in water or organic solvents. Commonly used reductants are borohydride, citrate, ascorbate, and elemental hydrogen (Ahmad et al. 2003). The reduction of silver ions (Ag^+) in aqueous solution generally yields colloidal silver with particle diameters of several nanometers. Previous studies showed that use of a strong reductant such as borohydride, resulted in small particles, but the generation of larger particles was difficult to control. Use of a weaker reductant such as citrate, resulted in a slower reduction rate, but the size distribution was far from narrow. Controlled synthesis of silver nanoparticles is based on a two step reduction process. In this technique a strong reducing agent is used to produce small particles, which are enlarged in a secondary step by further reduction with the aid of a weaker reducing agent (Lee and Meisel 1982). Different studies reported the enlargement of particles in the secondary step from about 20–45 nm to 120–170 nm. The synthesis of nanoparticles by chemical reduction methods is therefore often performed in the presence of stabilizers in order to prevent unwanted agglomeration of the colloidal silver in the solution of nanoparticles. To prevent the agglomeration of metallic nanoparticles, a stabilizing agent such as sodium dodecyl benzyl sulfate or polyvinyl pyrrolidone is also added to the reaction mixture. Generally, the chemical methods are low-cost for high volume; however, their drawbacks include contamination due to precursor chemicals, use of toxic solvents, and generation of hazardous by-products (Thakkar et al. 2010). There is an increasing need to develop high-yield, low-cost, nontoxic, and environmentally benign procedures for the synthesis of metallic nanoparticles (Mohanpuria et al. 2008; Rai et al. 2008; Sharma et al. 2009; Bar et al. 2009).

3.4.3 Biological Synthesis of Silver Nanoparticles

Chemical approaches are the most popular methods for the preparation of nanoparticles. However, some chemical methods cannot avoid the usage of toxic chemicals in the synthesis protocol. Since noble metal nanoparticles such as gold, silver and platinum nanoparticles are widely applied to human contacting areas and there is a growing need to develop environmentally friendly processes of nanoparticles synthesis that do not use toxic chemicals. Biological methods of nanoparticles synthesis using microorganism (Nair and Pradeep 2002), enzyme (Willner et al. 2006), and plant or plant extract (Shankar et al. 2004a, b) are suggested as possible eco-friendly alternatives to chemical and physical methods. Using plant for nanoparticles synthesis can be advantageous over other biological processes by eliminating the elaborate process of maintaining cell cultures (Shankar et al. 2004b). It can also be suitably scaled up for large-scale synthesis of nanoparticles.

In recent years, the development of efficient green chemistry methods for the synthesis of metal nanoparticles has become a major focus for researchers. They have investigated in order to find an eco-friendly technique for the production of well-characterized nanoparticles. Nanoparticles produced by plants are more stable and the rate of synthesis is faster than in the case of microorganisms. The advantages of using plant and plant-derived materials for biosynthesis of metal nanoparticles have influenced researchers to investigate mechanisms of metal ions uptake and bio reduction by plants, and to understand the possible mechanism of metal nanoparticles formation in plants (Iravani 2011).

3.5 Mulberry

Mulberry can grow in a wide range of climatic, topographical and soil conditions (Imran et al. 2010). It is well known that mulberry leaves are traditionally used for feeding the silkworm in the most parts of world (Adeduntan 2003). *Morus* plant species possess enormous importance in medicinal, economical, industrial, clinical, and domestic fields. Work carried out on some selected species of this plant demonstrates bioactivities for which plant has been used as folk medicine, *e.g.* mulberry fruit juice has been used as folk remedies for asthma, cold, cough, diarrhea, dyspepsia, edema, fever, headache, hypertension, and wounds. Roots and bark are purgative, anthelminthic, astringent, while leaves of mulberry play a vital role in rearing silkworm (Stalikas 2007). It is reported that mulberry leaf contains moisture, carbohydrates, and proteins that are utilized by silkworm larvae (Ghoush and Alam 2003).

The mulberry plant in the tropical belt is grown as a low bush while it is grown as a high bush in temperate regions. In tropical conditions, Individual leaf and branch harvest yields 10–30 tonnes/ha/year, while shoot harvesting in temperate regions has a leaf yield of 25–30 tonnes/ha/year. The percentage of moisture, protein and carbohydrates is higher in temperate regions when compared to the tropics. Mulberry is a monoecious, occasionally dioecious shrub or moderate-sized tree with a fairly cylindrical straight bole, up to 3.0 in high and 1.8 inches in girth. Leaves are very variable, ovate or broadly ovate, serrate or crenate-Serrate, and often deeply lobed. The plant is frost hardy but liable to Wind damage. It regenerates itself naturally from seeds that are dispersed by birds and to a limited extent by jackals and human beings. It can be propagated artificially by seeds or cuttings. It grows rapidly in the early stages and reaches maturity at an early age; the growth rate falls off rapidly after approximately 10 years. At present in many other parts of the world, mulberry leaves are predominantly used for silk production.

Numerous types of mulberry are under cultivation in various silk-producing countries of the world; the types differ in their adaptability to various soils and climates, resistance to diseases, food value of the leaf crop for the silkworm and suitability for use as stock or scion in grafting. In Japan, the world's major silk-producing country, approximately 700 types of mulberry are known to exist, of which 21 have been selected for extensive cultivation. Some of these types are adaptable to a wide range of climatic conditions. The most important type of mulberry grown in India for rearing silkworms is, *Morus alba* var. *multicaulis* Loud, which is a native of China or the Philippines.

India has the advantage of producing all the four known commercial silk varieties in the world. i.e. mulberry, tasar, eri and muga. Mulberry silk is domesticated while the rest are wild. India produces currently about 14050 tonnes of silk of which mulberry alone accounts for more than 90 % of the total silk production, practiced in over 60,000 villages in the country (Lakshmanan and Geetha 2000). The preferential food value of mulberry leaf for silkworm larvae is attributed to the presence of three stimulant factors, an attractant, a biting factor and a swallowing factor. The substances that attract the larvae to the leaves have been identified as citral, linalyl acetate, linalool, terpenyl acetate and hexenol. Sitosterol (approximately 0.2 % in leaves), together with some sterols and water-soluble substance are the main factor that stimulates the biting action.The major phenolic acids identified are gallic, protocatechuic, p-hydroxybenzoic, vanillic, chlorogenic, syringic, *p*-coumaric, ferulic and *m*-coumaric acids. chlorogenic acid is the prominent phenolic acid in all leaves samples collected from three mulberry species

Mulberry leaves are also useful as cattle fodder. They are nutritious and palatable and are stated to improve milk yield when fed to dairy animals. The feeding value of mulberry leaves is rated high by livestock owners. Feeding experiments have shown that up to 6 kg of leaves per day can be fed to milch cows without adversely affecting the health of animals or the yield and butter content of milk. Mulberry leaf stalks, left after feeding silkworms, can also be used for feeding cattle without any adverse effect on their health and performance. Mulberry leaves can also be used in poultry rations. Incorporation of shade-dried mulberry leaves in layers mash to the extent of 6 % showed an increase in egg production with desirable yolk colour without any adverse effect on body weight and egg quality (Narayana and Setty 1977). Mulberry leaves, owing to their high carotene content, can form a valuable source of vitamin A for the health of poultry birds and increased egg production.

3.6 Insect Model: *Bombyx mori*

The silkworm *Bombyx mori* has been domesticated for silk production for about 5000 years. There are many farms raising silkworms in many countries including China, India, and Thailand. The domesticated silkworm is not only an agriculturally important species with high economic value, but also a key model organism in Lepidoptera especially for genomics research (Nagaraju and Goldsmith 2002). In addition, it is used as an important bioreactor for the production of recombinant proteins (Tomita et al. 2003). The ease with which the silkworm can be handled and reared makes it the most suitable model for laboratory research besides the fruitfly, *Drosophila*.

The silkworm is a monophagous insect that mainly feeds on fresh mulberry leaves. Artificial diet for the silkworm is studied and applied extensively in Japan, China and some other countries as it contains essential nutrients for supporting the normal growth of the larva. Although artificial diet can obviate the serious drawbacks of mulberry leaves such as the seasonal limitation on supply of fresh leaves, possible harm from parasites or pesticides and high labour cost, the silkworms reared on artificial diet during all instars are not as good as those fed on fresh mulberry leaves, which are reflected in many aspects such as the filament quality of cocoons, survival rate of young larvae, and resistance to bacterial and viral diseases (Kataoka and Imai 1986; Zhou et al. 2008)

The fifth instar is a transition period for metamorphosis from larva to pupa, and for biosynthesizing and spinning, during which larvae take-in almost the entire nutrition for the whole life process. Day 3 of the fifth instar is found to be a boundary for larval development. (Grzelak 1995). Most biological processes may be similar before this time point, but after that, silkworms begin to synthesize silk proteins in mass. Among all the body tissues of silkworm, midgut, hemolymph, fat body and posterior silk gland are the vital tissues during the growth and development of silkworm, which function in nutrient digestion and absorption, nutrient transportation and innate immunity, nutrient synthesis and storage, and fibroin synthesis, respectively (Zhou et al. 2008).

India holds a unique place in the world silk market as it supplies all the four commercial varieties of silk, mulberry silk from the mulberry silkworm, *Bombyx mori*, Eri silk from Eri silkworm, *Samia Cynthia ricini*, Tasar silk from the Tasar Silkworm, *Antheraea mylitta* D. and *Antheraea proyeli* and Muga silk from Muga silkworm, *Antheraea assamia.*

3.7 Toxicity Assessment in Silk Worm *Bombyx Mori*

Improving the quality and quantity of silk by using mulberry leaves enriched with organic and inorganic supplements as feed for silkworm is tried by many workers (Ito and Niminura 1966; Subburathinam and Krishnan 1998). Sarker et al. (1995) reported the growth of larvae of *Bombyx mori* significantly improved when fed on mulberry leaves supplemented with different nutrients such as soya milk, milk powder, vitamins, and potassium iodide salts.

Mulberry leaves soaked in cobalt solution (100 μg/ml) enhanced the body weight and increased the number of eggs laid by the adult (Chakrabarti and Medda 1978). Chamundeshwari and Radhakrishnaih (1994) reported that larvae fed with zinc or nickel sprayed mulberry leaves (1 mg/10 g wet weight), once in each instar upto 4th instar and in alternate days of 5th instar, increased the weight of larvae and silk gland. It also shows effects on economic parameters *i.e*, the cocoon length, width, shell weight, shell ratio, filament length and weight was observed. These are very much significant in the larvae fed with zinc sprayed leaves than nickel sprayed leaves.

The effect of zinc treatment at different doses 1, 10, 50 and 100 ppm on silkworm 5th instar larvae was tried by Balamani et al. (1995) and reported that it enhances the silk quality by 50 % compared to the control group left untreated. Saha and khan (1995) reported that leaves supplemented with nickel chloride appreciably increased the lipid content in treated silkworm, *Bombyx mori* at 0.25 and 0.50 % concentrations. However at higher concentrations (0.75 %) the reverse results were obtained.

Saha and khan (1996) reported that enrichment of mulberry leaves with multivitamins and multimineral capsules at various concentrations (0.08, 0.16, 0.32 and 0.64 %) reduced the larval and pupal periods and the reproductive potential was enhanced at these concentrations. Even the highest concentration *i.e* 0.64 % of these capsules had deleterious effects on all parameters. Changes in the protein metabolism in the hemolymph and fatbody of the 5th instar larvae was observed, following the exposure to sublethal concentration of fenitrothion and ethion (Nath et al. 1997).

The effect of administering different quantities of JHA (6,7- epoxy-3-ethylphenoxy)-7-methylnonae), orally to last instar larvae of *Philosamia ricini* was studied by Singh (1990). Prolongation of the life of the larval instar followed by death, imperfect ecdysis affecting cocooning and pupation, non-viable larval-pupal intermediates with very thin cocoons are observed.

The first ever observation on hemolymph protein is made by Lauffer (1943) on silkworm, *Bombyx mori. L.* The composition of free amino acid in the hemolymph and the influence of dietary amino acid on hemolymph is studied by Inokuchi (1970). Any change in feeding, immediately reflects in hemolymph protein of lepidopteron larvae, because hemolymph performs several physiological functions such as transport and storage reserve (Ayyangar and Rao 1990). The concentration of proteins and carbohydrate in developing embryos and larval hemolymph of Tasar silk is described by Sinha and Sinha (1994). A progressive increase in protein content is observed in larval development reaching maximum in the 5th instar larvae.

Most drug candidates obtained by *in vitro* screening are inappropriate as medicines due to problems of toxicity and their pharmacodynamics in humans. Preclinical tests in animal models are essential for evaluating the therapeutic effects of drug candidates for further development. Mammals, such as mouse, rat, marmot, rabbit, dog, and monkey, are commonly used as drug-screening models to examine the pharmacodynamics of chemicals. The use of mammals for drug development is expensive and highly problematic with regard to ethical issues (Orlans et al. 1998; Baumans 2004). The development of invertebrate animals as drug-screening models will overcome these problems. Invertebrate animals such as *Romalea microptera* (Johny et al. 2007), *Caenorhabditis elegans* (Mahajan-Miklos et al. 1999), and *Drosophila melanogaster* (Lemaitre et al. 1996; Bernal and Kimbrell 2000) are generally used in bacterial infection models. A limitation of these models is that their body size are too small for using in studies of pharmacodynamics. The silkworm's body size is large enough for hemolymph preparations and organ isolation, which are essential for studying the pharmacodynamics of drugs in animal bodies. Thus, we propose the use of silkworms as model animals for evaluating the therapeutic effects of drug candidates (Hamamoto and Sekimizu 2005).

3.8 Nanotoxicology

Nanotoxicology is a new field established in the current decade, which emphasizes the usage of nanomaterial in commercial goods and novel technologies, which is generating several risk factors to the human health and environment. Though the ingestion level of nanoparticles is very low in the living systems and their toxicity level is also estimated to be very less, these nanomaterial leads to the accumulation in their host, it may explicit the adverse effect later. At one stage the accumulation of nanoparticles may become an eco hazard. It has been already reported that nanomaterials such as carbon nanotubes, quantum dots and metal and metal oxide nanoparticles are having the adverse toxic effects when they are dosed even in low level (Asharani et al. 2009). The earlier reports insist that biologically synthesized nanoparticles were safer materials which don't have any corrosiveness to the living host and also they do not create any potential danger. Though the biological nanoparticles are harmless, the biocompatibility of their usage can be evaluated through the *in vivo* and *in vitro* toxicity studies in the model animals. These assessments of toxicity mediated by bionanoparticles will open up several questions raised against the risk assessment in human and cattle. The experimental evidence may bring out a decline in the use of nanomaterial in several aspects such as nano medicine, material safety, nano coupled drug, nano commercial goods. So the present investigation is sketched to analyze the toxicity created by biological SNPs in which the chosen model animal was silkworm, *Bombyx mori* and same has reflected towards the nanoparticle treatment (Figs. 3.1 and 3.2 (Pandiarajan et al. 2016))

Toxicity evaluation on silkworm, *Bombyx mori* are reasonably comparable to those of other lepidopteran pest, so it is considered as a suitable model for exploring effects of any new synthetic formulations for the past two deacades (Rajathi et al. 2010). Silkworm rearing is a traditional business in Tamil Nadu and the life of many people depends on it. Increase in larval growth and cocoon quality and quantity would result better economics for this industry and meet the production needs. Consequently, the enrichment of mulberry leaves by supplementary compounds with the aim of increasing the production of cocoon is a very important aspect.

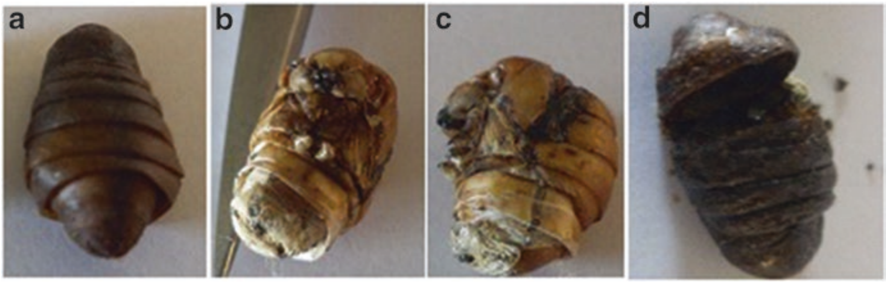

Fig. 3.1 Effect of silver nanoparticles (10 ppm and 100 ppm) on pupation in silkworm, *Bombyx mori* subjected to oral feeding from day 1 to day 4 of fifth-instar (**a**) control, (**b**) 1 ppm, (**c**) 10 ppm; (**d**) 100 ppm (Pandiarajan et al. 2016)

Fig. 3.2 Effect of silver nanoparticles on the phenotype of the adult silkworm, *Bombyx mori* subjected to oral feeding from day 3 to day 5 of fifth-instar. (**a**) control adult; (**b**) 1 ppm treated adult; (**c**) 10 ppm adult with wing deformities; (**d**) 100 ppm adult with wing deformities (Pandiarajan et al. 2016)

Many investigations have been done on this topic and various reports have been published (Etebari et al. 2004; Islam et al. 2004). Copiously the earlier reports have mentioned that the silver Nanoparticles can be utilized as an ancillary complex which can boost up the growth and development of the larvae and also the quality and quantity of the cocoon.

Silk worm, *Bombyx mori* is a monophagous insect, which feeds only mulberry leaves. So the *Morus alba* was elected for the biosynthesis of phyto coupled nanoparticles, at the same time this will also clearlyelucidate toxicity twisted by nanoparticles. *Morus alba*, Mulberry leaves are rich in protein and amino acids, and there is a high correlation between leaf protein levels and the production efficiency of the cocoon shell, *i.e*., the cocoon shell weight is relative to the total amount of mulberry leaves consumed by the silkworm (Machii and Katagiri 1991). It is therefore possible that an increase in the protein level of mulberry leaves may lead to improvement in cocoon productivity. Consequently, the enrichment of mulberry leaves by supplementary compounds with the aim of increasing the production of cocoon is a very important aspect. The leaves have some obvious benefits for humans. They contain various minerals and extracts, such as beta-carotene, GABA-1, amino acids, carotenoids, flavonoids, chlorophyll, vitamin C, B1, B2, B6, A and they are rich in fiber. Many investigations have been done on this topic and various reports have been published (Etebari et al. 2004; Islam et al. 2004).

Nutrition plays an important role in improving the growth and development of the silkworm, *Bombyx mori L.* like other organisms. Nutritional quality of mulberry leaf has greater importance on regulation over the quantum of digestibility of food among silkworms. It is direct relation with growth and silk production in silkworms. Such nutritional requirements in food consumption have direct impact on the overall physical and genetical traits such as larval and cocoon weight, quantity of silk production, pupation and reproduction. Silkworm nutrition refers the substances required by silkworm for its growth and metabolic functions and obtained from ingested food remaining other nutritional components are being synthesized itself through various biochemical pathways including proteineous silk fibre of commercial interest. Research on silkworm, *Bombyx mori* clearly demonstrates that nanoparticle could

Table 3.1 Showing the weight increase at larval stages of *Bombyx mori* during different dosage of treatment at 24 h interval (10 larvae – chosen for study)

Weight of the larvae (10) (in g)				
Contents	Day 1	Day 2 After 24 h	Day 3 After 48 h	Day 4 After 72 h
Control	21.77	26.23	27.20	26.95
1 ppm	21.77	27.19	30.88	28.44
10 ppm	21.77	25.20	28.66	27.80
100 ppm	21.77	26.73	28.31	27.80
LE	21.77	25.44	27.94	25.94

Table 3.2 Showing the weight of total pupa and cocoon (shell) at pupal stage of *Bombyx mori* during different dosage of treatment at 24 h interval

Weight of the pupa + cocoon (2 insects) (in g)						
Contents	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
Control	3.02	2.52	2.7	2.60	2.56	2.23
1 ppm	2.70	3.05	3.20	2.86	2.95	2.34
10 ppm	3.29	2.82	3.13	2.68	2.69	2.25
100 ppm	3.22	3.37	3.07	2.55	2.53	2.72
LE	2.97	3.14	3.11	2.33	2.60	2.14

stimulate more production of fibroin protein which can help in producing carbon nanotube in future (Bhattacharya and Mukherjee 2008). Legay (1958) has states that silk production is dependent on the larval nutrition and the nutritive value of mulberry leaves that play effective role in producing good quality cocoon.

3.8.1 In Vitro *and* In Vivo *Nanotoxicity*

The rapid expansion in the field of nanotechnology is likely to benefit the society; yet there are increasing concerns that human and environmental exposure to nanoparticles and nanomaterials may produce adverse effects. Due to their small size and high surface area, coupled to other physiochemical properties such as metal contaminants, coatings and charged surfaces, and quantum related effects, introduction of nanomaterials into the environment may have unexpected consequences, both beneficial and harmful. The harmful aspects are as follows:

During our investigation the fifth instar larvae were fed with leaves supplemented with silver nanoparticles with varying concentrations (1 ppm, 10 ppm, 100 ppm) (Figs. 3.1 and 3.2). Observations were made on the larval and cocoon characters (Tables 3.1, 3.2, 3.3 and 3.4 and Figs. 3.3, 3.4, 3.5 and 3.6). Maximum larval weight was observed in 1 ppm Silver nanoparticles treatment (2.888 g) as compared to control (2.679 g). Marked increase in cocoon weight was found in silver nanoparticles (1.465 g) treatment. Minimum cocoon weight (1.319 g) was recorded in control. The results observed with respect to pupal weight was found to be maxi-

Table 3.3 Showing the weight of pupa (alone) of *Bombyx mori* at larval treatment stage with different doses at 24 h intervals

Weight of the pupa (in g)						
Contents	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
Control	2.53	2.06	2.10	2.02	2.04	1.83
1 ppm	2.17	1.99	2.61	2.26	2.26	1.83
10 ppm	2.67	2.14	2.60	2.28	2.19	1.75
100 ppm	2.74	2.81	2.51	2.01	2.01	2.23
LE	2.44	2.66	2.48	1.89	2.17	1.70

Table 3.4 Showing the weight of shell of pupa (alone) at different dosage of treatment during larval stage of *Bombyx mori* at 24 h intervals

Weight of the cocoon shell (in g)						
Contents	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
Control	0.43	0.39	0.51	0.41	0.40	0.38
1 ppm	0.45	0.63	0.53	0.53	0.52	0.49
10 ppm	0.50	0.45	0.51	0.40	0.48	0.46
100 ppm	0.46	0.51	0.51	0.50	0.49	0.38
LE	0.50	0.51	0.52	0.44	0.41	0.42

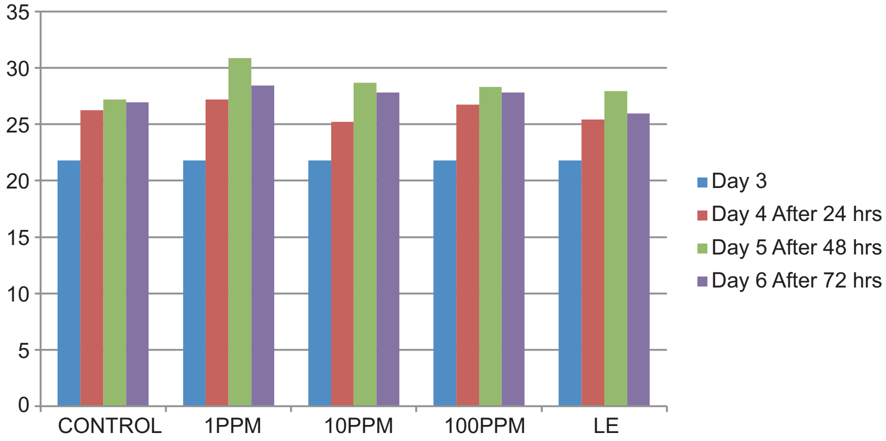

Fig. 3.3 Showing the weight increase at larval stages of *Bombyx mori* during different dosage of treatment at 24 h interval

mum (1.206 g) in 100 ppm silver nanoparticles treatment with minimum pupal weight was obtained in control untreated group (1.067 g). Maximum shell weight (4.97 g (20 cocoons)) was observed in treatment with 1 ppm, followed by 10 ppm (4.77 g), 100 ppm (4.76 g) treatment respectively. Least shell weight was observed with the control (4 g). Significant increase in shell ratio was observed in treatment with 1 ppm (16.95 %) as compared to control (15.92 %) (Tables 3.1, 3.2, 3.3 and 3.4 and Figs. 3.3, 3.4, 3.5 and 3.6).

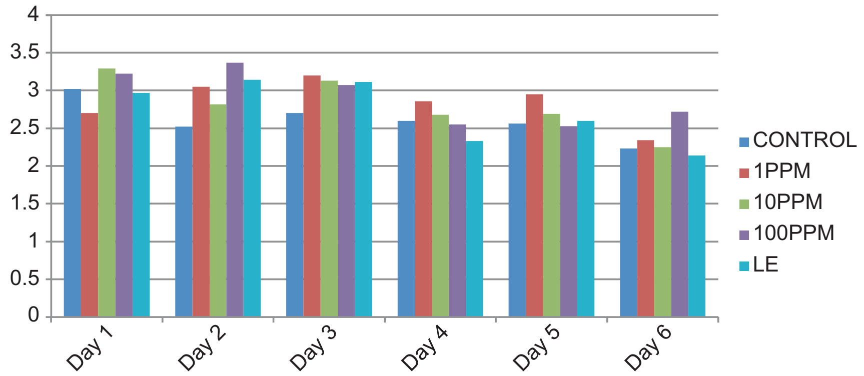

Fig. 3.4 Showing the weight of total pupa and cocoon (shell) at pupal stage of *Bombyx mori* during different dosage of treatment at 24 h interval

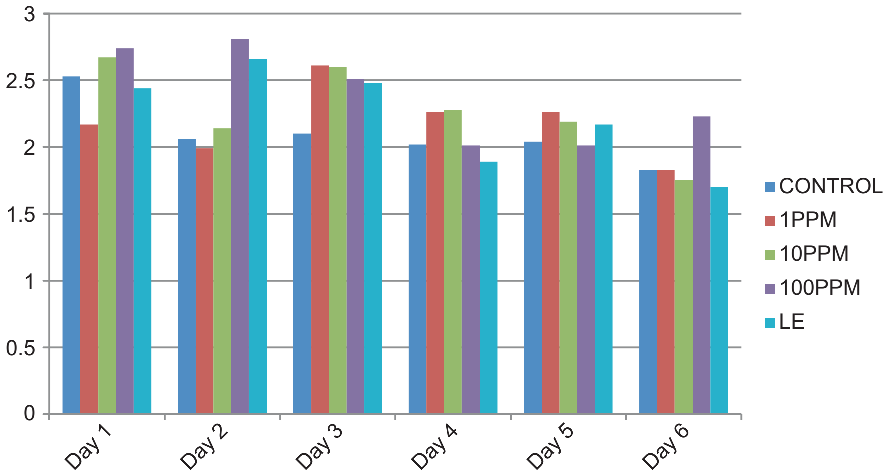

Fig. 3.5 Showing the weight of pupa (alone) of *Bombyx mori* at larval treatment stage with different doses at 24 h intervals

3.8.2 Unicellular Animals

Silver NPs revealed high toxicity against the prokaryotic and eukaryotic organisms. The toxicity of the silver NPs is reported in unicellular eukaryotic organism *Paramecium caudatum* and some bacterial strains (Kvitek et al. 2009).

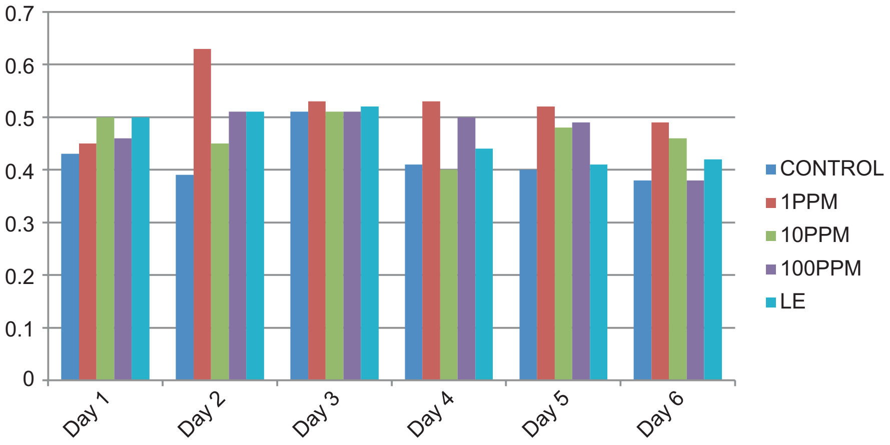

Fig. 3.6 Showing the weight of shell of pupa (alone) at different dosage of treatment during larval stage of *Bombyx mori* at 24 h intervals

3.8.3 Nanosilver Disrupt Soil Microbial Communities

Information on the toxicity of terrestrial and sediment organisms is limited, but is slowly being investigated. Again toxicity appears to be dependent on physico-chemical soil properties and sediment properties. There is currently very little research on the effect of silver nanoparticles on soil microbial communities *in situ*, that is, in real soils. But *in situ* studies have demonstrated that silver, even in larger particle form, inhibits microbial growth below concentrations of other heavy metals (Murata et al. 2007). It is especially toxic to heterotrophic (ammonifying/ nitrogen fixing) and chemolithotrophic bacteria. Chemolithotropic bacteria belong to the lithotropic family of microbes and consume inorganic material. These organisms liberate many crucial nutrients, and are essential in the formation of soil. Ratte (1999) showed that silver ions inhibit enzymes needed for nitrifying bacteria. The toxic effect of silver on bacteria also appears to disrupt denitrification processes, with the potential to cause ecosystem-level disruption (Throback et al. 2007). Denitrification is a bacteria-driven process where nitrates are converted to nitrogen gas in some soils, wetlands and other wet environments. A denitrifying bacterium plays an important role in removing nitrate from water contaminated by the usage of excessive fertilizer. Denitrification is important because excess nitrates reduce plant productivity and can result in eutrophication (an unhealthy increase in nutrients) in rivers, lakes and marine ecosystems, and are a drinking water pollutant.

3.8.4 Aquatic Life

Currently little is known about the fate of silver nanoparticles in the environment. However depending on their surface structure and shape, silver nanoparticles may have different reactivity. Silver nanoparticles also act as a reservoir of silver ions and may release Ag^+ ions continuously. Silver is toxic to fish, crabs, algae and other water plants, as well as nitrogen fixing bacteria (Albright and Wilson 1974). Of which, special importance may be the effect of silver on lithothrophes, organisms that play an important role in the digestion of inorganic material and creation of soils.

Aquatic organisms differ significantly in their sensitivity to silver. The accumulation of silver and its toxicity depends on and varies with environmental conditions such as salinity and pH. Research into the toxicity of nanosilver to aquatic organisms is still limited and tends to focus on a small number of key species – zebra fish, invertebrates, some algae. Toxicity of silver is a result of silver ions and depends on their concentration. Silver ions react with thiol (a molecular group that includes a bonded sulfur and hydrogen atom (-SH) in biomolecules). For instance, in fish, silver ions block the active absorption of sodium and chlorine as well as causing sublethal effects (Hogstrand and Wood 1996). In water fleas silver ions disturb ion regulation via a competitive inhibition of Na^+ (sodium) uptake.

The freshwater invertebrates, *Ceriodaphnia dubia* and *Daphnia magna* are not only standard testing organisms for aquatic toxicity testing, but they are also one of the most sensitive organisms to silver. Naddy et al. (2007) showed that chronic exposure of *D. magna* and *C. dubia* to silver resulted in decreased growth and reproduction (8.80 and 2.65 mg dissolved silver/l), and complete mortality at higher levels. It is well known that silver ions in the natural environment tend to form stable complexes both inorganic (e.g. chloride, thiosulphate and sulphide) and organic (monomeric thiols and natural organic matter). Silver thiosulphate was thought to be relatively inert. However Hiriart-Baer et al. (2006) showed that silver thiosulphate complexes can be transported across cell membranes in *Chlamydomonas reinhardtii* and *Pseudokirchneriella subcapitata* (two freshwater algae species), and leads to increased toxicity.

Navarro et al. (2008) investigated the toxicity of silver nanoparticles versus silver ions to *Chlamydomonas reinhardtii*. Based on total silver concentration, the silver ions appeared to be 18 times more toxic than the nanosilver particles. However the closer inspection revealed that when compared to a function of silver concentration, the silver nano particles appeared more toxic than the silver ions. The researchers reasoned that silver nanoparticles contributed to the overall toxicity of silver to the algae by providing a continuous source of silver ions.

The release of silver nanoparticles into fresh water ecosystems can lead to more biological, physical, and chemical irrecoverable impacts on the ecosystems and their fishes (Kalbassi et al. 2011). Silver ions are known to be one of the most toxic metals to freshwater fish. However, their effect is often mediated by a variety of agents (e.g. chloride) present in water (Grosell et al. 2000). Silver ions are the most potent gill toxicant in freshwater fish. The toxicity of nanosilver particle appears to be independent from silver ions. Griffitt et al. (2009) found that when zebra fish was exposed to nanosilver particles, the silver level in their gills increased. Gene expression proofing suggested that the silver nanoparticles interacted with the gills in a different manner than soluble silver particles and hence the observed effects were not due to silver ions.

Silver nanoparticles administered *in vivo* to zebra fish embryos increased deformation rates and, ultimately, led to death. Individual silver nanoparticles were found inside embryos at each developmental stage (Lee et al. 2007). Scown et al. (2010) evaluated the effects of silver NPs in fish, rainbow trout (*Oncorhynchus mykiss*) were exposed via the water to commercial silver particles. It is reported that exposure of silver NPs to rainbow trout at concentrations close to current estimations of environmental levels can result in accumulation of silver in the gills and liver of fish and can affect likely oxidative metabolism in the gills. Significant inhibitions of growth and reproduction of daphnia were observed when the daphnia exposed to silver nanoparticles (Zhoa and Wang 2011).

3.9 Bioaccumulation of Silver Nanoparticles

Silver nanoparticles present in consumer goods are released into the environment, where they could be bioaccumulated or enter the food chain/drinking water supplies (Karn et al. 2009; Gao et al. 2009). The environmental fate of nanosilver will depend upon the nature of the nanoparticles. The bioavailability of these materials can be determined by their uptake when they are in contact with organisms.

The uptake of silver nanoparticles is relatively fast and time-dependent. Usually after 24 h of exposure, the vast majority of cells contain silver nanoparticles. Sometimes, uptake saturation is observed after prolonged incubation (Lu et al. 2010; Mahmood et al. 2010). Silver nanoparticles uptake can be influenced by several factors, such as morphology of nanoparticles, their size, concentration and surface properties (Mailander and Landfester 2009). Impact of Silver nanoparticles depends not only on their dose but also on their size (Lankveld et al. 2010).

Sardari et al. (2012) suggested that the effect of nanosilver particles on the tissues may cause organ toxicity in rats. Accumulation silver nanoparticles showed tissue damages, bloodshed, cell necrosis and apoptosis in rats.

3.9.1 Skin

Silver nanoparticles are widely used in medicine, physics, material sciences and chemistry. Many medical products are coated or embedded with nanosilver, for example surgical instruments, bone prostheses and dental alloys. Being present in consumer goods, silver nanoparticles can easily penetrate the human body through different portals, for example, silver nanoparticles released from different surface coatings can readily be inhaled (Panyala et al. 2008) or can be directly from medical devices, such as catheters or dental and bone implants (Chen and Schluesener 2008). Silver nanoparticles present in dressings for burns and ointments are used for wound healing, nanosilver–based textiles and cosmetics (like antibacterial deoderents) as they can penetrate into skin (Arora et al. 2008; Samberg et al. 2010) and localize in stratum corneum and the upper layers of epidermis (Larese et al. 2009).

3.9.2 Digestive System

Nanoparticles can be entered in to the body via oral route by water, food, cosmetics, drugs, drug delivery devices, etc. Shahare et al. (2013) assessed the oral exposure of AgNP on the mucosa of the small intestine in mice. The study revealed that significant decrease in body weight of mice in AgNP treated mice. The main function of small intestine is absorption. Due to the loss of microvilli of enterocytes, the absorptive surface area of the intestine was markedly reduced which led to decrease in the absorption of nutrient materials resulting in a reduction in the body weight of mice.

3.9.3 Circulatory System

Tang et al. (2009) examined the ability of silver nanoparticles and silver microparticles to traverse the brain blood barrier. Silver nanoparticles crossed the blood brain barrier only after subcutaneous injection and they caused neuronal degeneration/necrosis. All effects were time dependent, reaching a plateau after 12 weeks.

The role of the cardiovascular system in silver nanoparticles distribution and discrimination in the body was subsequently examined. A high percentage of silver nanoparticles, but not microparticles, is translocated to the blood circulatory system after their subcutaneous administration and was deposited in all main organs (kidneys, liver, spleen, brain and lungs). Ultra structural observations confirmed silver nanoparticles accumulation in renal tubular epithelial cells, hepatocytes and neurons. Human erythrocytes when exposed to different concentration of starch coated silver nanoparticles (25–400 μg/ml) shows deleterious effects when compared to cells exposed to uncoated silver nanoparticles within 3 h of exposure (Asharani et al. 2011).

European perch (*Perca fulviatilis*) was treated with varying concentrations of silver nanoparticles and silver nitrate separately. From which it was found that silver nanoparticles treated group didn't show any adverse effect on basal metabolic rate, whereas European perch treated with silver nitrate alone resulted in significant increase in basal metabolic rate (Bilberg et al. 2010). Silver nanoparticles affect early development of zebra fish (*Danio rerio*). Developmental retardation, increased heart rates, neuro developmental effects, sluggish circulation, pericardial edema, tube heart and eye malformation are observed resulting from embryonic exposure to silver nanoparticles (Wu et al. 2010).

3.9.4 Respiratory System

Takenaka et al. (2001) observed the pulmonary and systemic distribution of inhaled ultrafine elemental silver (EAg) particles in rats. The inhaled silver nanoparticles were also observed in the liver, kidney, spleen, brain, and heart in low concentrations.

3.9.5 Excretory System

In fischer F344 rats, more adverse effects including loss of body weight, changes in blood biochemical parameters, bile duct hyperplasia, fibrosis and accumulation of silver nanoparticles in kidney are observed in cells treated with 30, 125 and 500 mg/kg of silver nanoparticles (Kim et al. 2010).

3.9.6 Reproductive System

Silver nanoparticle accumulation is also affect the reproductive system. Roh et al. (2010) reported that accumulation of silver nanoparticles induced reproductive failure in *C. elegans* and that oxidative stress. Gromadzka-Ostrowska et al. (2012) tested the effects of different sizes and doses of nanosilver (AgNP) on male rats. Sperm count, germ cell DNA damage and seminiferous tubule morphometry were measured after the intravenously administered low dose of small AgNP. Silver nanoparticles also caused changes in sperm counts and the study suggested a genotoxic effect of low dose small size AgNP.

3.10 Apoptosis

Studies revealed that accumulation of nanoparticles very toxic to cell. Nanoparticles enter to the cell via endocytotic routes and cause various types of cell injury through free radical reactions.

Gopinath et al. (2010) reported that small sized uncoated silver nanoparticles (18 nm) at concentration 11 μg/ml, induced P^{53} mediated apoptosis in baby hamster kidney (BHK21) and human colon adenocarcinoma (HT29) cells. Li et al. (2010) observed and reported embryonic toxicity in mouse blastocysts when exposed to silver nanoparticles (25 and 50 μM).

Samberg et al. (2010) evaluated the toxicity of silver nanoparticles in human epidermal keratinocytes both *in vitro* and *in vivo*. Here the cells are treated with different concentrations of uncoated and carbon coated silver nanoparticles separately. Dose dependent decrease in viability of cells is observed in cells treated with uncoated silver nanoparticles whereas no toxic effect is observed in the cells treated with carbon coated silver nanoparticles.

Arora et al. (2008) reported the reduced cell viability, oxidative stress, DNA damage and higher CASP3 activity in HT-1080 human fibrosarcoma cells (derived from dermis) and A431 human skin carcinoma cells (derived from epidermis) when treated with silver nanoparticles.

As with many substances at the nanoscale, the toxicity of nanosilver is greater than that of silver in bulk form; silver is comparatively more toxic than other heavy metals when it is in nanoparticle form (Braydich-Stolle et al. 2005). Physical characteristics of nanomaterials, such as their size, shape and surface properties, can exert a toxic effect that goes beyond that associated with their chemical composition (Brunner et al. 2006). For instance, Hussain et al. (2005) demonstrated that nanoparticles of silver produce reactive oxygen species (ROS), which may result in oxidative stress-mediated toxicity. Production of ROS, highly reactive molecules which include free radicals, can interfere with cellular metabolism, cause inflammation and damage proteins, membranes and DNA. Reactive oxygen species production is a key mechanism for nanomaterials toxicity (Nel et al. 2006). Chae et al. (2009) evaluated the toxic impact of silver nanoparticles on Japanese medaka (*Oryzias latipes*) and reported that exposure of Ag-NPs led to cellular and DNA damage, as well as carcinogenic and oxidative stresses, genes related with metal detoxification/metabolism regulation and radical scavenging action were also induced.

3.11 Both Silver and Nanosilver Are Toxic

3.11.1 DNA Damage

In adult zebra fish, there is evidence of the uptake of silver nanoparticles through the gills that caused silver nanoparticles- specific changes in gene expression and resulted in increased mortality. Increased mortality upon treatment with silver nanoparticles was observed in adult Japanese medaka (*Oryzias latipes*), accompanied by induction of DNA damage (Wu et al. 2010). Treatment of rainbow trout (*Oncorhynchus mykiss*) with silver nanoparticles caused an increase in expression of Cytochrome P450 1A2 (*cyp1a20)* in the gills (Grosell et al. 2000).

3.11.2 Cell Division in Plants

Kumari et al. (2009) investigated cytotoxic and genotoxic impacts of silver nanoparticles using root tip cells of *Allium cepa* as an indicator organism. It is suggested that silver nanoparticles could penetrate plant system and may impair stages of cell division causing chromatin bridge, stickiness, disturbed metaphase, multiple chromosomal breaks and cell disintegration. It is also suggested that plants as an important component of the ecosystems need to be included when evaluating the overall toxicological impact of the nanoparticles in the environment.

Nematodes are widely found in soils and play a critical role in the soil food web. Their functions include primary production, decomposition, energy flow, and nutrient cycling. Nematode abundance also serves as a useful indicator in natural ecosystems to the presence of soil pollutants and ecological disturbances. Several toxicity tests have indeed been developed for this purpose, but Wang et al. (2009) was the first to investigate the effect of metal oxide nanoparticles on nematodes (*C.elegans*).

3.12 Conclusion

Every person is exposed to nanometer sized foreign particles; we inhale them with every breath, and consume them with every drink. In truth, every organism on Earth continuously encounters nanometer-sized entities. Nanoparticles are defined as a small object that behaves as a whole unit in terms of its transport and properties. Nano science is an emerging field that deals with interaction between molecules, cells and engineered substances such as molecular fragments, atoms and molecules. In terms of size constraints, the National Nanotechnology Initiative (NNI) defines nanotechnology in dimensions of roughly 1 to 100 nanometers (nm). But in broader range it can be extended up to 1000 nm. Nanotechnology can be defined as the design, synthesis, and application of materials and devices whose size and shape have been engineered at the nanoscale. It exploits unique chemical, physical, electrical, and mechanical properties that emerge when matter is structured at the nanoscale. Silver has been valued throughout history for many of its properties that are useful to humans. It is used as a precious commodity in currencies, ornaments, jewellery, electrical contacts and photography, among others. One of the most beneficial uses of silver has been as a potent antimicrobial agent that is toxic to fungi, viruses and algae. Silver has long been used as a disinfectant; for example, the metal has been used in treating wounds and burns because of its broad-spectrum toxicity to bacteria as well as because of its reputation of limited toxicity to humans.

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Chapter 4
Nanoparticles for Agriculture: Synthesis, Classification and Characterization

G. Madhumitha, J. Fowsiya, and Selvaraj Mohana Roopan

Abstract Nanotechnology is a promising for agriculture and food products. Here we review the synthesis, classification and characterization of nanoparticles. Nanoparticles, nanoemulsions, nanopores and nanoproducts have found applications such as identification of diseases by nanosensors, pesticide and fertilizer improvement by nanoformulation, packaging and processing of food industry.

Keywords Nanoparticles • Classification • Synthesis • Characterization • Agri-food uses

4.1 Introduction

In the past few years technical, social tasks and new goals are challenges in agriculture and food processing using various nanomaterials. Science and technology have been continually increasing the abilities of new materials to lightweight ultra – strong materials for space uses and new components for developing solar panels to produce radiation resist materials for construct nuclear power plants. In addressing all the challenges and goals of today's and future research work and social tasks which includes developed welfare, healthcare, global climate change, good security and highly production of vital materials, nanotechnology has been achieved a great applications in twenty-first century (Kathy 2014). Nanotechnology is a novel technology with more advances in the field of materials such as nanoparticles, nanopowder, nanolayer and nanodevice etc. (Fig. 4.1). The term nanotechnology was introduced by Nori Taniguchi in 1974 at Tokyo international conference and he proposed a lecture on "Ultrafine machining: the processing of a material to nanoscale precision". His work was focused on machining hard and brittle material such as quartz crystal, silicon, alumina and ceramics by ultrasonic machining. Nanoparticles

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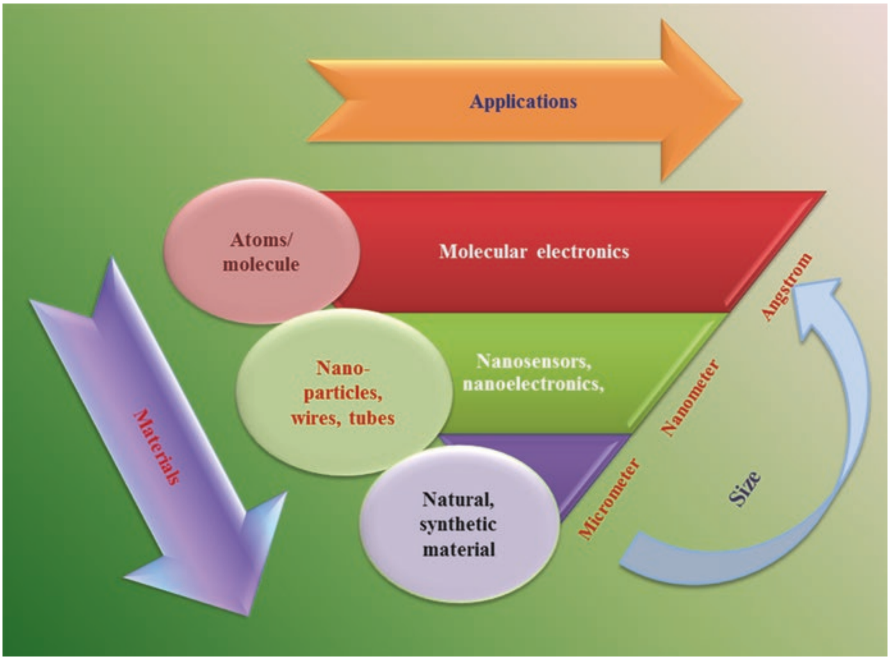


Fig. 4.1 Nanostrucutured engineering application

give an important novel application to the nanotechnology and reveals optical, magnetic and electrical properties (Hahens et al. 2007).

The term “Nano” was derived from the Greek word Nanos which means “dwarf” and it can be represented by 10^{-9}, i.e., one billion of any unit. The first generation (late 1990s-early 2000s) of nanotechnology was developed in performance of micro materials and the second generation was started in the significant of nanoparticles such as clusters, nanocrystalline and multilayers etc., Therefore, to summarize nanotechnology is a complex interdisciplinary science that include Nanochemistry, Nanophysics, Nanomaterials science, Nanoelectronics, Optoelectronics, Nanoengineering, Nanobionics, Nanometrology, Nanodevice building and Nano hand craft.

Nanoparticles defined as a set of substance that contains at least one dimension is less than 100 nm (Fig. 4.2). A nanometer is one millionth of a millimeter approximately 100,000 times smaller than human hair (Kathy 2014). Nanoparticles are designed at nanometer size to provide novel properties. The reason behind the different properties of nanoparticles is increase in the surface area and new quantum effects. The greater surface area and new quantum effects leads to the greater chemical reactivity, strength, novel optical, electrical and magnetic behaviors (Shalini et al. 2012).

The small size of the nanoparticles exhibits different and most useful physical and chemical applications than bulk materials. Due to the increase in surface area in nanostrucutres, increase the significant effect in melting point, chemical reactivity,

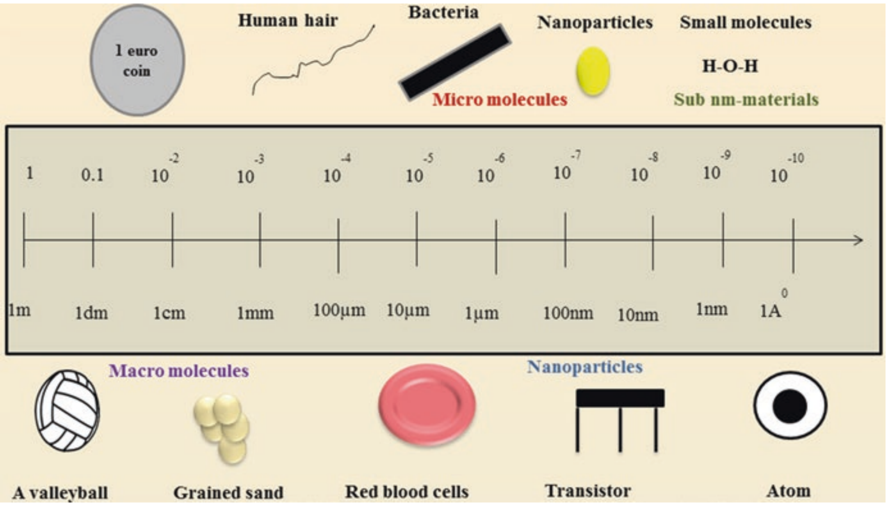


Fig. 4.2 Nanoparticles size ranges from 1 to 100 nm - pictorial representation

catalytic activity, fluorescence and conductivity properties. On the other hand, increasing the surface energy of material generally decreases the size of a particle. The size of the nanoparticles can be divided into internal or intrinsic size effect and external size effect as well as classical and quantum effects. The internal or intrinsic size effect is defined as the change in the property of particles such as lattice parameters, chemical reactivity, melting point, hardness and band gap, etc., External size effects are interaction between physical field and matter. The external size effects are comparable with a length of physical phenomena including coherent length, screening length etc., the quantum size effect arises in the variation of plasticity, thermal conductivity and diffusion etc., In turns to the quantum size effects occurs in elecroconductivity in magnetic field, oscillation of the superconductivity critical temperature and in the generation of hypersound. However, the size and property of nanoparticles are different from those of atoms and bulk materials which are similar to the properties of micro materials. From the size of nanoparticles, we can conclude that nanoparticles may be classified as zero dimensions (i.e. atomic clusters, filaments), one dimension (Multilayer), two dimension (Ultrafine grained overlayers or buried layers) and three dimensions (Nanophase materials) (Johnson 2003; Mikami et al. 2013; Meng and Xiao 2014; Ozin and Arsenault 2009). Hence, size of the particles characterize the nanoparticles into different types and its plays an important role in its synthesis and application (Fig. 4.3).

Apart from the other application of nanoparticles, it became more important in agriculture since it has been addressing the large scale inherent imperfection that need in flexible nanoparticles. The major problem with the global food production is increase in use of pesticides and fertilizer without affecting to the environment. Nanoparticles in food and agriculture field aimed many applications for food production at global level. It was developed in different way to enhance the food production, water treatment, targeted treatment, improve the ability to take nutri-

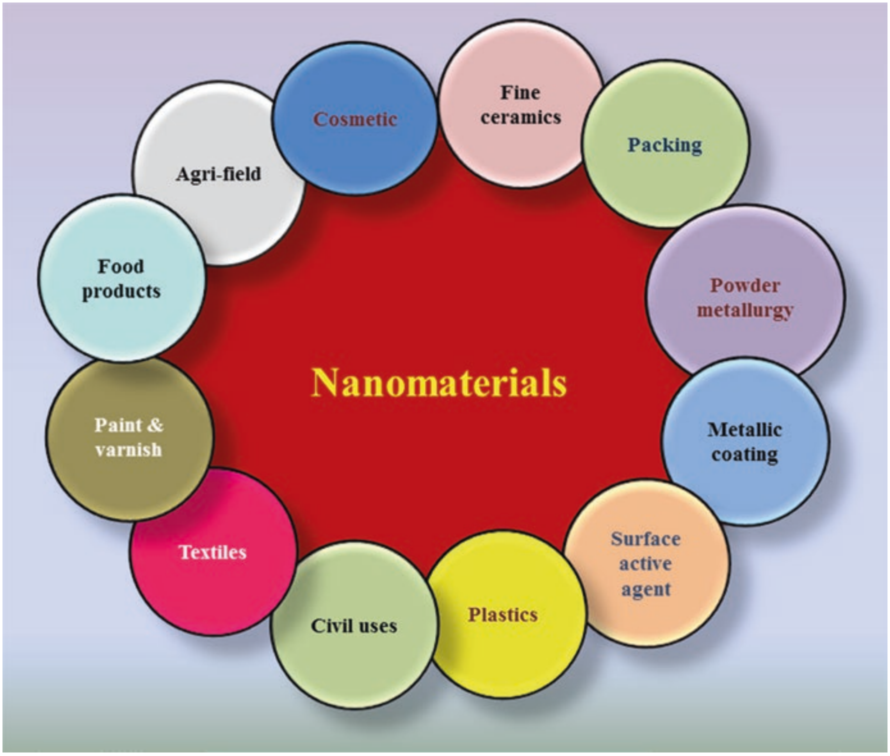


Fig. 4.3 Nanomaterial application in various fields

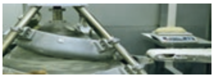
ents, diseases detection, preservation (Table 4.1) and packaging of food (Sharon et al. 2010). In the case of food applications, nanoparticles develop a new plastic for food packaging. Oxygen is the problematic factor causes food spoilage and discoloration. Nanoparticles are used in this type of problem and it has been found to be zigzag direction in plastic to prevent the diffusion of oxygen as a barrier.

In this book chapter we will further introduce the reader to the field of nanoparticles and its classification, synthesis, characterization and nanoparticles applications in agriculture and food processing.

4.2 Gleiter's Classification of Nanoparticles

The nanoparticles was classified by controlled influence of the structure on the atomic level and may be divided into three categories. In the first categories, nanoparticles are reduce in dimensions or dimensionality of isolated or fixed nanometer sized particles, thin wires or thin films. The Chemical vapor deposition (CVD) (Chira and Abhijit 2012), physical vapor deposition (PVD), various aerosol techniques and precipitation from the vapor and supersaturated liquid or solids methods

Table 4.1 Nanomaterial application in agri-food industry

 Agriculture	 Food processing	 Food packaging	 Supplements
Nanocapsules used to deliver pesticides, fertilizers and other agrichemicals more efficiently	Nanocapsules improve bioavailability of neutraceuticals in standard ingredients such as oil	Fluorescent nanoparticles detect foodborne pathogens	Absorption of nutrients can enhanced by nanosize powder
Nanosensors used to monitor soil conditions and crop growth	Nanoparticles used as gelation and viscosifying agents	Nanosensors used to maintain temperature and time	Cellulose nanocrystals used as drug carrier
Detection of animal and pathogen can be detect by nanosensors	Nanoemulsion and particles are good for nutrients availability and dispersion	Nanoclays and nanofilm used to prevent food spoil	Better absorption and stability by nanoencapsulation
Nanocapsules use for vaccine delivery	Nanocapsules enhance flavor.	Nanoparticles can used for antimicrobial and antifungal property	Deliver nutrients without affection color and taste of food
DNA delivery can be done by using nanoparticles	Nanoparticles can bind and remove pathogens and chemicals from food	Modified permeation behavior of foils	Nanodroplets for better absorption

are general methods to prepare this kind of nanoparticles and in past few decades it has been used as catalyst and semiconductors due to well-structured arrangement or microstructure of atoms. The second category nanoparticles are defined as nanometer microstructure which is limited to thin layer of bulk materials and it can be prepared in wide range by PVD, CVD and laser beam treatment methods (Subhash et al. 2012). These types of methods were applied to alter the chemical composition and physical properties. In turns to the third category, it comprise the bulk solids in nanometer scale microstructure. The chemical composition and atomic size or arrangement of the crystallite was formed by the bulk solids on a length of nanometer throughout the bulk.

Therefore, from the results of material science, it was concluded that most of the solids are depends on the microstructure, the spatial dimension and crystallographic directions of particles within a structure generally changes the physical properties. Hence, there is a need of classification in which nanoparticles were depends on the number dimensions lies in the nanometer size. Nanometer size materials can be classified into three types of category based on the number of dimensions such as zero dimensional structures (0D), one dimensional structure (1D), two dimensional structures (2D) and three dimensional structures (3D) (Dutta et al. 1995). Figures 4.4 and 4.5 represents the schematic diagram of generally classified nanoparticles and dimensionally classified nanoparticles.

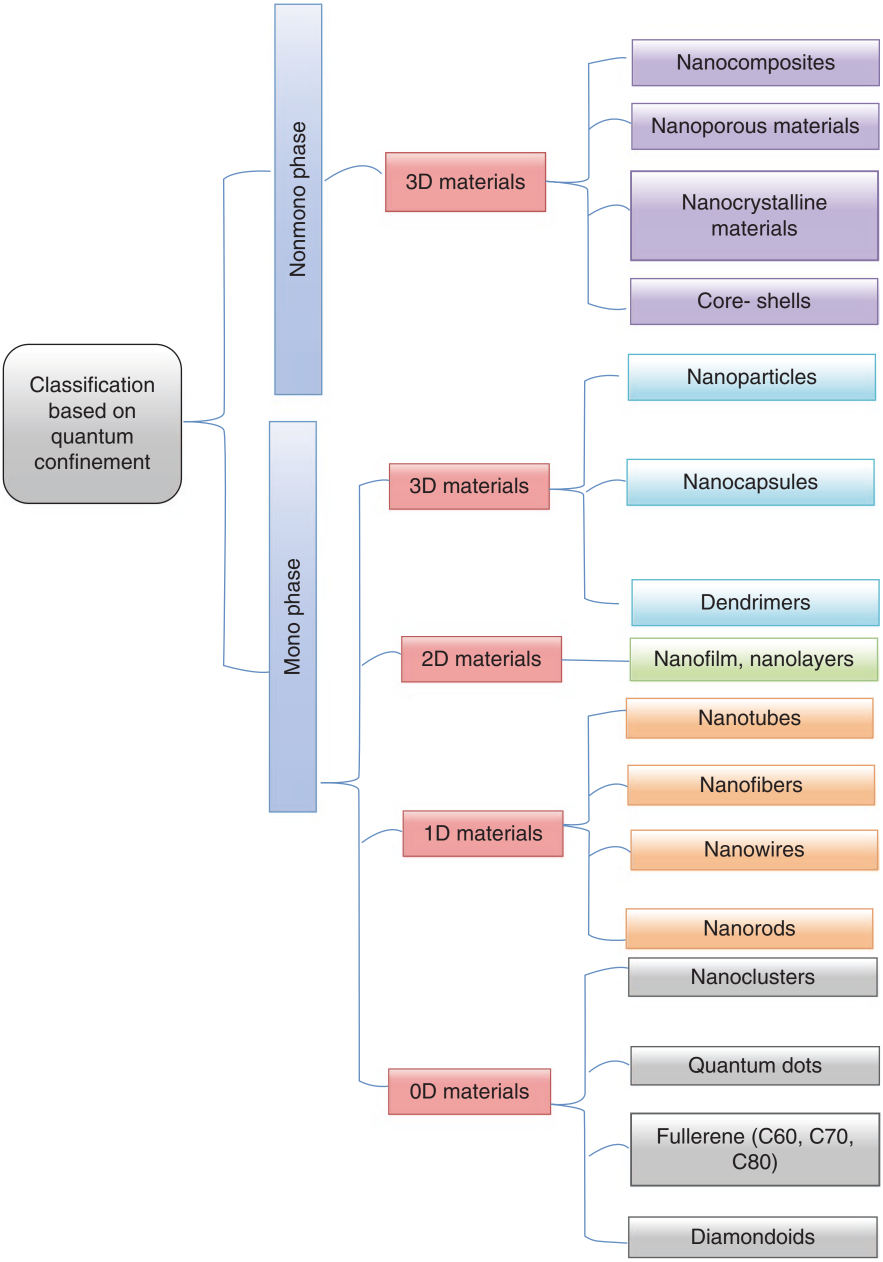


Fig. 4.4 Classification of nanomaterials based on dimensionality

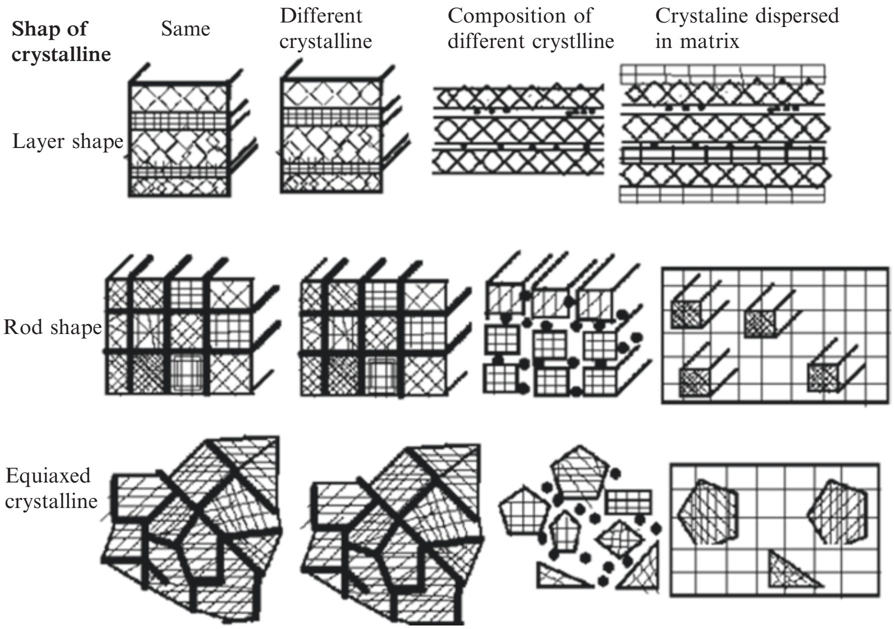


Fig. 4.5 Gleiter's classification of nanoparticles

4.2.1 Zero Dimensional Nanoparticles

Zero dimensional structured analogous is the simplest building block for the designing of nanoparticles that have less than 100 nm. The examples for 0D are nanoparticles, nanoclusters, nanocrystals. In the past few years, there was a significant development was made in the field of 0D nanoparticles. Recently, 0D nanoparticles such as quantum dots (uniform particles), nanoparticles, heterogeneous particles arrays, core shell quantum dots, hollow spheres and nanolenses have been synthesized by many research groups (Kim et al. 2010; Zhang and Wang 2008; Gautam et al. 2005; Lee et al. 2009). Nanoparticles are generally defined as Zero dimensional nanosized building blocks or amorphous which possess irregular shape in 1–100 nm. A nanoparticle includes metallic, metal oxides, nanostructured metal oxides. The metallic nanoparticles have different physical and chemical properties from bulk metal properties that have been proved in various applications. On the other hand, nanocluster is a grouping of nanoparticles in 1–10 nm size and narrow size distribution. Nanocluster is an intermediate state of matter lies between molecules and solids. Nanoclusters can be found in two main sources namely gas aggregation source and supersonic nozzle source. Gas aggregation source utilizes the property of atoms in inert area and generated vapors introduced into cold inert gas at high pressure. In the case of supersonic nozzle source, metal was vaporized and mixed with inert gas at 75–1500 K. Then it was allowed into nozzle into high vacuum. As far we have defined the zero dimensional nanoparticles, nanocrystals also one kind of nanoparticles which is less than 100 nm in single or poly crystalline arrangement of atoms. Due to the smaller size of the nanocrystals, it can provide more efficient light emission than the bulk and larger crystals (Burt 2005; Tiwari 1996). A special group was found in the nanocrystals that is comprised of a semiconductors is known as quantum dots in 2–10 nm size range. These are widely used as semiconductors, insulators, metals, magnetic materials, metallic oxides, optoelectronic devices, information storage and colored coded quantum dots also used for DNA testing. Increase in the surface area of quantum dots, it has gained a wide range of applications in therapeutic agents for simultaneous drug delivery, in vivo imaging and tissue engineering. Generally quantum dots can be referred to the quantum confinement of electrons and it carries a hole in very small dimensional than Bohr radius. Mostly nanocrystals, composed from the group II and VI or II and V group (Larson et al. 2003) (Fig. 4.6).

For example, the nanoparticles can exists in different forms like ultrafine, agglomerates and aggregates. The nanoparticles surface is related to nano, carbon nanotubes, nanosilver, nanogold, nanocopper, nanozinc oxide and nanotitinum oxide etc. If the rice husk is burnt, it will form large amount of nanosilica. This nanosilica generally used as source material nutrient in agricultural field.

4.2.2 One Dimensional Nanoparticles

The second class of classification of nanoparticles is one dimensional nanoparticles which can be defined as having at least one dimension in 1–100 nm range size. These are a thin films or monolayer (1–100 nm) which is used as electronic devices in past decades. More recently thin film layer has been used in the field of solar cells, catalysis, different technological applications, chemical and biological sensors, information storage systems, fibre-optic systems, magneto-optic and optical devices.

Nanofiber, nanowire, and nanorods are a few examples for one dimensional nanoparticle. Nanofiber is defined as fibers with less than 100 nm size and it can be prepared by melt processing, interfacial polymerization and electrostatic spinning. Inorganic nanofibers also can be prepared by many techniques and mostly ceramic materials with nanofiber such as titanium oxide, silicon oxide, zirconium oxide etc.,

Nanorods are lies between 1 and 100 nm sizes. It can be synthesized from metal or semiconductors materials by chemical methods. The main potential application of nanorod is its reflectivity in display technologies due to its orientation change in presence of electric field (Ayala et al. 2005). However, one dimensional structure has large number of phenomena at nanosclae and dimensionality. Hence, it can be differentiating by their functional properties and morphological studies (Figure 4.7).

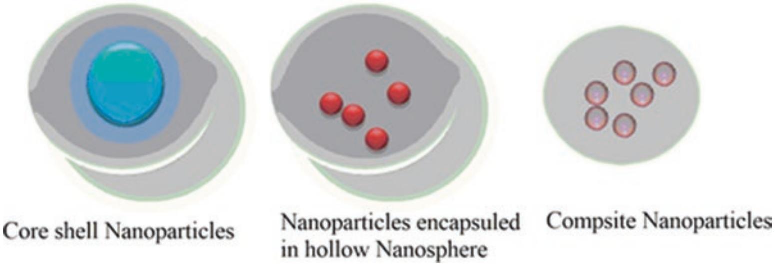


Fig. 4.6 Examples for zero dimensional nanoparticles

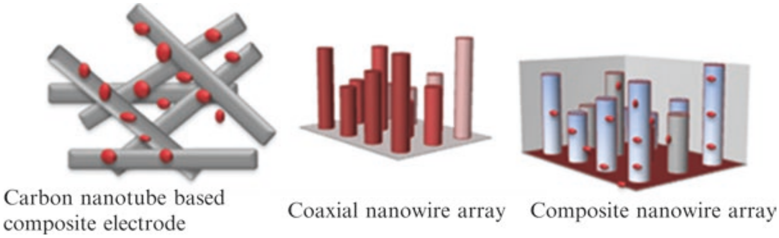


Fig. 4.7 One dimensional nanoparticle

4.2.3 Two Dimensional Nanoparticles

2D nanostructures have two dimensions outside of nanometric size range and it has been gained more applications in materials science research due to its low dimensional properties which is different from the bulk materials properties. Due to its certain geometries display unique shape dependent properties, 2D nanoparticles used as building block for nanodevices and also used in sensors, photocatalyst, nanocontainers, nanoreactors, and building component for some 2D nanoparticles (Kim 2009). Nanoprism, nanoplates, nanosheets, nanotubes, nanowalls and nanodisks are a few examples for 2D nanoparticles (Tiwari et al. 2008; Siril et al. 2009; Vizireanu et al. 2010). Most interestingly carbon nanotubes are hexagonal network of carbon in 1–100 nm length rolled up with graphite layer. It can be divided into two categories such as single walled carbon nanotubes having diameter close to one nanometer and Multi-walled carbon nanotubes which consists of multiple rolled layers of graphene. Heterostructures, nanolayer and nanodisks also one type of reduced 2D structures are believed to migrate from micro to nano electronics. However their unique properties can be determined by electromagnetic waves propagation based on Bragg diffraction law and the arrangement of atoms are quantum, same time 2D crystals in which the various quantum state and resonance effects are expected. These heterosturctures are monolayers of multiple 2D materials stacked vertically layer by layer and strictly restrict the migration of charged

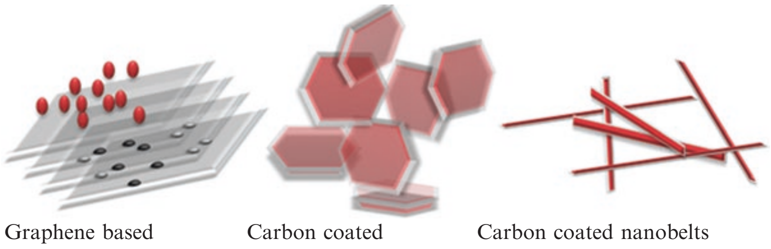


Fig. 4.8 Two dimensional nanoparticles

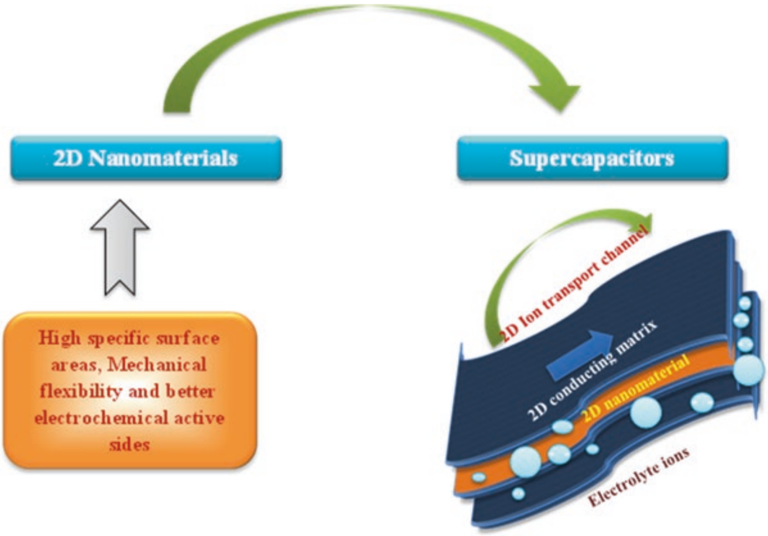


Fig. 4.9 Conductivity property of two dimensional nanoparticles

carriers forcing them into quantum confinement. Few examples for 2D and its conducting property is shown in Figs. 4.8 and 4.9.

4.2.4 *Three Dimensional Nanoparticles*

Three dimensional (3D) nanoparticles has been achieved by considerable research interest in past 10 years because of its remarkable large surface area and unique properties over their bulk counterparts arising from quantum size effect. However 3D nanoparticles behavior and applications are completely depends on the size, shape, dimensionality and morphologies. High surface area and good absorption

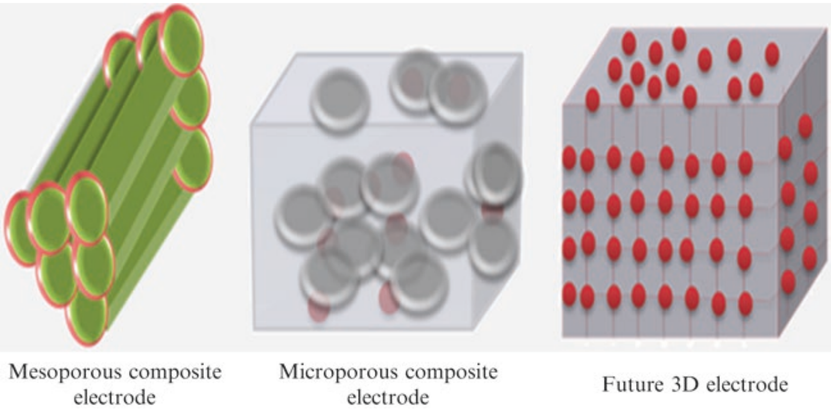


Fig. 4.10 Three dimensional electrodes

capacity of these nanoparticles attracted towards in the field of catalysis, magnetic materials and electrode materials (Fig. 4.10) for batteries as well as leads to the better transport of the molecules (Shen et al. 2008; Lee et al. 2006). Nanoballs (Dendritic structure), nanocoils, nanocones, nanopillars and nanoflowers are some examples for 3D nanoparticles. Fullerenes are spherical cages structure containing 28–100 numbers of carbons resembles like a soccer ball and composed with interactions of pentagons and hexagons. When the fullerenes subjected under high pressure, it can be comes into its original shape after regain of pressure. The molecules present in the fullerenes does not overlap or interact with each other, thus it gained more advantages to use as lubricants. Since, a fullerene is like biological active molecules which made up with empty dimensions. These empty dimensions can completely filled with several substrates for their potential medical applications (Tomalia 2004). Dendrimers are new class of nanoparticles in controlled structure polymers with nanometer dimensions. These are the basic building block units for the synthesis of organic and inorganic nanoparticles with 1–100 nm. Dendrimers has several applications including anti-inflammatory, antimicrobial, antiviral drugs, screening agents for high throughput drug discovery. Instead of all the advantages Dendrimers has few disadvantages because its affect the cell membrane as a result of positive charge on their surface (Macke et al. 2004).

4.3 Techniques for Synthesis of Nanoparticles

The physical, chemical, electronic and magnetic properties of nanoparticles became an important point of view in nanotechnology and nanostructured engineering. Several techniques have been developed to synthesize 0D, 1D, 2D and 3D nanoparticles in particular size, shape, dimensionality and structure. Hence, the discuss on physical and chemical methods for synthesize nanoparticles is very important.

4.3.1 Physical Methods

0D, 1D, 2D and 3D nanoparticles can be synthesized and fabricated by physical methods because of its eco-friendly path. Physical method is being top-down approach which begins with particular starting material ends with desired materials. Top-down method (Fig. 4.11) is ball milling, the formation of nanoparticles building blocks via mechanical erosion of the bulk materials. Large scale of nanometer size devices can be prepared by the controlled direct milling and fabrication which leads to the formation of massive solids into smaller and smaller portions, successively reaching the nanometer size. The various methods to synthesize nanoparticles will be discussed in more detail below.

4.3.1.1 Evaporation Technique

The evaporation technique (Fig. 4.12) is common method of thin film deposition and there is much evaporation technique including thermal and ion assisted evaporation for synthesis of nanoparticles. Inert gas evaporation technique is most common and widely used method to synthesis single phase metals and ceramic oxides. Evaporated molecules and gas molecules lose their energy via collision on evaporation methods which leads to the formation of homogeneous condensation of clusters (Seigel et al. 1988).

4.3.1.2 Sputtering Technique

Researchers have been developed various Sputtering technique namely, ion assisted deposition, ion beam (Richard 2006), and high power impulse magnetron (Ehiasarian et al. 2002) and gas flow sputtering (Ishii 1989)were used to synthesis nanoparticles (Fig. 4.13). Generally this method involves ejection of atoms or molecules or clusters to highly focused inert gas such as helium or argon.

4.3.1.3 Lithography Process

This type of method is rapidly used, effective and easy method to improve the synthesis of different dimensional nanoparticles with different substrate. In this method atoms or molecules transferred from a photomask on substrate surface to made many copies from one exposure. Lithography process divided into two main categories based on the fabrication. The first one is nonconventional method such as soft nano-imprint lithography, nanosphere lithography and colloidal lithography and other one is conventional process namely, e-beam lithography and focused ion beam lithography.

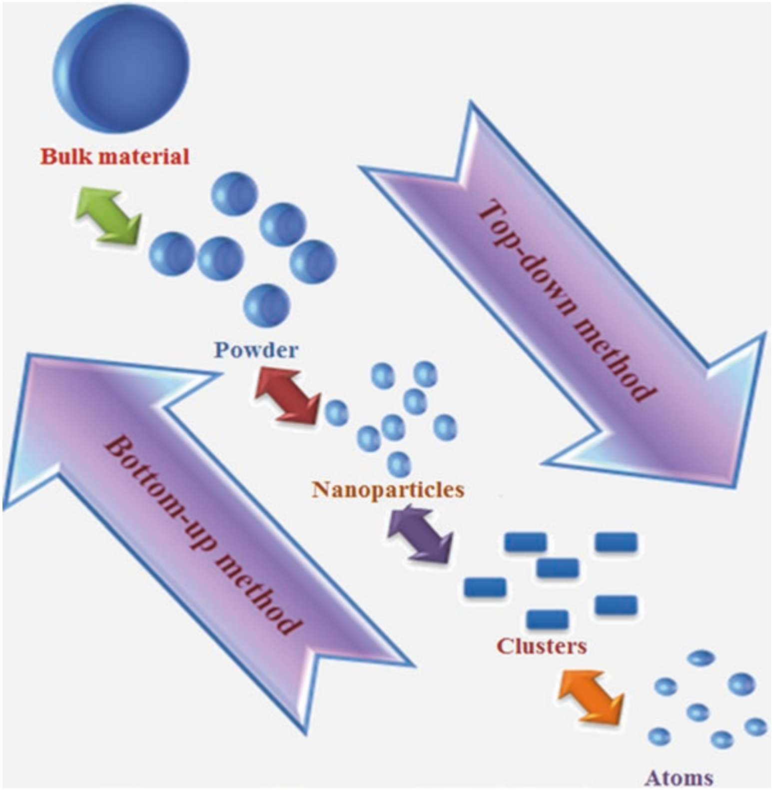


Fig. 4.11 Top-down and bottom-up approaches

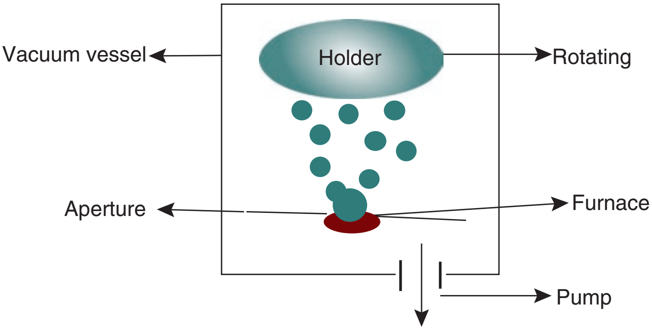


Fig. 4.12 Thermal evaporation technique

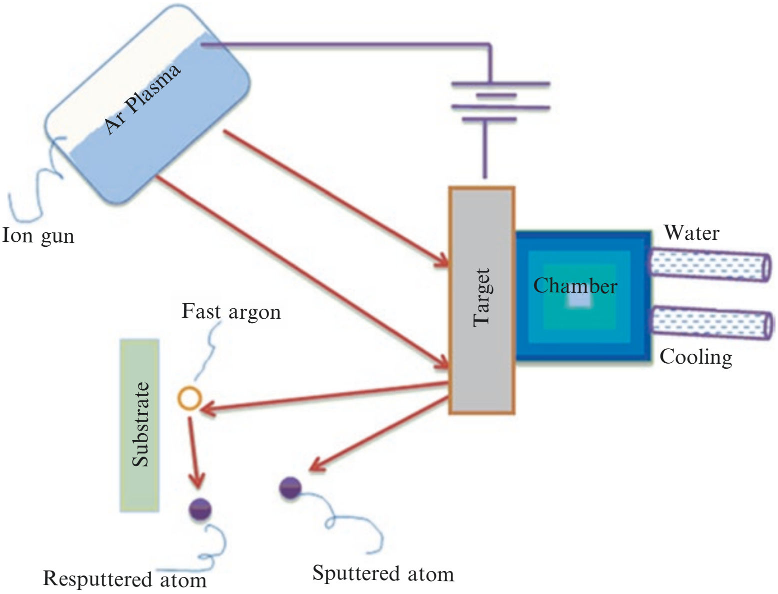


Fig. 4.13 Schematic diagram of sputtered system

4.3.1.4 Hot and Cold Plasma

When the plasma is fully ionized it is known as hot plasma and if the gas ionized in small fraction it is called as cold plasma. Generally in cold plasma also the temperature will be in high degree Celsius. An arc melting chamber and a collecting system will be present in typical equipment and pure arc metals allows more thin films alloys in an inert gas atmospheres. These thin films alloys can be prepared in bulk materials by arc melting chamber even at low temperature. For example silicon oxynitride nanowires were synthesized on nickel coated crackers as substrate (Feinberg and Gross 1974).

4.3.1.5 Spray Pyrolysis

Spray pyrolysis process is eco-friendly, low cost method than other film deposition process and it is used to synthesis nanoparticles, in which nanoparticles were deposited by spraying a solution on substrate to form chemical compounds. The main goal of this method is, no need for the pure substrate, chemicals, high cost vacuum equipment and exotic gases (Perednis et al. 2005).

4.3.1.6 Pulsed Laser Ablation

Pulsed laser ablation became very popular to the manufacture of high purity and ultra-fine nanomaterials via gas phase process. In this method reagent gas was filled in a chamber by controlled condensation and the materials were evaporated using pulsed laser. The materials will starts to diffuse on substrate to interact with the gas to form desired compounds such as oxides in the case of oxygen, nitride in the case of nitrogen or ammonia, carbide in the case of methane etc. This pulsed laser ablation method is widely used to synthesis metal compounds in chamber and it makes possible to prepare nanoparticles of mixed composition.

4.3.2 Chemical Methods to Synthesis Nanoparticles

Synthesis of nanoparticles by chemical method has been played an important role in the field of nanoparticles technology. Chemical method gives more advantages to prepare nanoparticles in desired nanometer size and structure. The first advantage of chemical method is to synthesis new materials that can be developed into the final products. On the other hand, the most advantage of chemical method is, it offers mixing of chemical compounds in molecular level. Still, this method involves some toxic chemicals and solvents and as well as forming byproducts that will require purifying the nanoparticles. Chemical process is based on the principle of bottom-up approach (Fig. 4.10), in which atoms or molecules assemble to form nanometer materials.

4.3.2.1 Lyotropic Liquid Crystal Templates

Lyotropic liquid crystals is widely used method whose lattice constants range from several nanometer to tens nanometer which may become perfect template for designing novel nanoparticles. Hexagonal, bicontinuous and lamellar phases are Lyotropic liquid crystals (LLC) templates that have more advantages in synthesis of materials with nanometer size dimension and anisotropic morphologies with several applications including drug delivery, catalysis, material chemistry and tissue engineering. The Poly (butadiene)-poly (ethylene) gels in cubic, hexagonal phases are stable in mechanical and chemical aspects. Long chain affects the nucleation and growth of the products that might be controlled to synthesis nanoparticles with desired size, structure and orientation. The LLC templates are confine the structure of nanoparticles particularly depends upon the interaction of inorganic ions and surfactants with in the templates. Hence, by changing the concentration and composition of LLC, it is possible to control the morphology of desired materials.

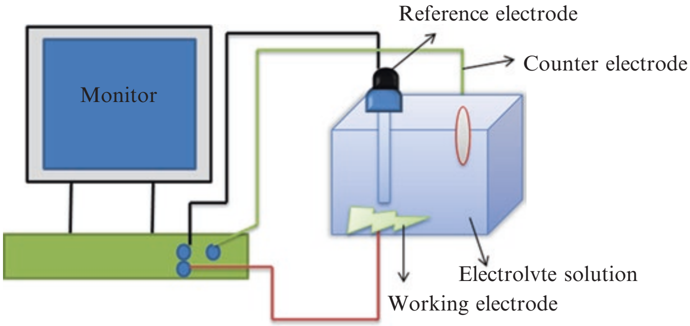


Fig. 4.14 Electrochemical deposition method setup

4.3.2.2 Electrochemical Depositing Process

Generally electrochemical deposition process involves with two or three electrode for electric current to deposit a composite layer nanostructure containing materials on surface of the substrate. The basic principle behind this method is, inducing chemical reactions in an aqueous electrolyte solution with applied voltage, e.g. this is the method of using current to coat electrically conductive materials with thin layer of metal. Electrochemical depositing process is very attractive method because the process is simple and effective. It has no limitation as far as sample shape and size concerned. This method is combined with bottom-up and top-down approaches. A thin platinum wire, saturated calomel electrode and sample, reference and working electrode are the parts were used (Fig. 4.14). The higher and lower potential, potential on time and off time are main four parameters that influence the platinum electrode (Zhang et al. 2010).

4.3.2.3 Hydrothermal and Solvothermal Technique

Both hydrothermal and Solvothermal process are similar to each other, but the difference is precursor solution is usually not aqueous, but it is not always. Solvothermal method allows for the precise control over size, shape distribution, better quality, growth of large number of crystals and crystallinity metal oxide nanoparticles. Change in the some parameters such as temperature, time, solvent type, surfactant type and precursor type, it is possible to control the size and structure of nanoparticles. The hydrothermal system can be defined as the use of water as reaction medium in a sealed reaction container when temperature is raised above 100 °C. Basically it is used in the synthesis of crystals which solubility depends on water minerals under high pressure. The crystal growth was carried out in an autoclave, in which a nutrient is applied along with water. The temperature gradient is attached to the opposite side of the growth vessel. Thus, the hotter end dissolves the nutrient, cooler and causes compounds to addition growth (Saravanan et al. 2008).

4.3.2.4 Sol-Gel Process

The sol gel technology offers possibility to form novel, predefined properties for materials in colloidal chemistry technology. The sol terms represents the colloidal solution made up of solid particles in nanometer dimensionality. The sol gel process is also known as chemical solution deposition is a wet process that can be used to synthesis nanoparticles by gelation and precipitation. The first step includes the preparation of precursor solution that affect the refractive index, hardness and other properties of resulting materials. Precursor might be inorganic, but more often metal organic precursors are used. The precursor is dissolved in alcohol then water to undergo hydrolysis and polymerization reaction to form a colloidal suspension. After the preparation of precursor solution is condensation reaction in which particles condense in the gel phase resulting in porous gel. The gel can be further modified with dopants for better properties of materials (Madhumitha et al. 2015). Sol gel technology and its byproducts shown in Fig. 4.15.

4.3.2.5 Chemical Vapor Deposition

The chemical vapor deposition process is a chemical method in which gaseous atoms or molecules transform into a solid material on the surface of the substrate. The typical chemical vapor deposition method involves five methods, they are, (i) well mixed gases and diluent inert gas are placed into a chamber at controlled flow rate, (ii) the gas species moves towards the surface site, (iii) reactant gets adsorbed on the surface area, (iv) reactants undergoes chemical reaction with substrate to form desired nanoparticles and (v) gaseous reaction products will desorbed and banished from the chamber (An et al. 2010).

4.4 Characterization Techniques for Nanoparticles

For analysis and characterization of nanoparticles recently several methods were introduced including microscope, diffraction techniques, spectroscopies and electric and magnetic measurements. Generally the optical microscope gives micron level materials characterization with more resolution. But magnification of materials cannot be achieved by optical microscope due to aberrations and limit in wavelength of light. Thus, imaging analysis like scanning electron microscope (SEM), transmission electron microscope (TEM), scanning tunneling microscopy (STM), and Atomic force microscopy (AFM) gives more advantages to observe sub-micron size materials. However the principle of the all these techniques are different but one common thing is that they give highly magnified image of the surface or the bulk of the materials. Basic principle and the applications of the imaging techniques in characterization of nanoparticles are described below.

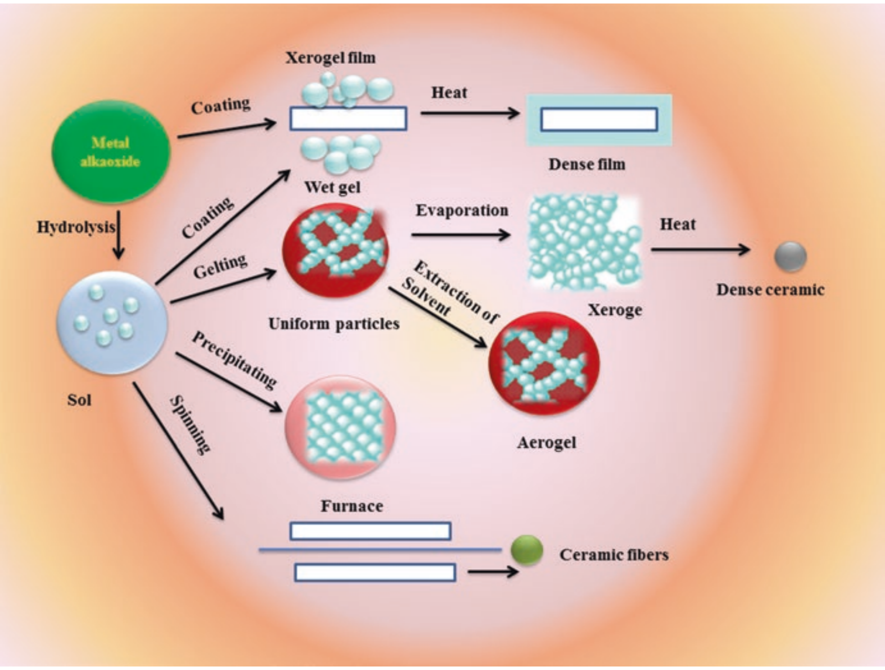


Fig. 4.15 Sol gel process

4.4.1 *Scanning Electron Microscopy*

Scanning electron microscopy (SEM) is an electron microscope which gives high resolution images of nanoparticles by scanning the surface of materials with high energy beam of light. In the conventional light microscope light waves were bend in glass lenses and generate images of materials whereas in the case of SEM creates the magnified images by using electrons instead of light waves (Joshi 2008).

4.4.1.1 Principle of Scanning Electron Microscopy

When a beam of electron passes through the surface of the specimen and interacts with the atoms or molecules of the sample, the beam is collimated by lenses of electromagnetic condenser and scanned across the surface of the sample by electromagnetic deflection coils. The collection of the secondary electron that are released form the sample is the first or primary imaging method and this secondary electrons were detected by scintillation materials that can able to produce flashes of light from electron that can be detected by photomultiplier. The image of the materials can form by correlating the sample scan position with resulting signal. The SEM can give very high resolution images of the sample surface about 1–5 nm. Detection of signal, amplification of signal can be done by electronic devices and it will display the images on a cathode ray in which the faster scanning is synchronized (Fig. 4.16). SEM requires a conductive specimen to scan the surface of object by electron beam and that electron has a path to ground for conventional imaging. In the case of non-conductive specimen a layer of conductive materials has to be coated by low vacuum sputter coating or high vacuum evaporation (Nixon 1971).

The SEM shows more resolution three dimensional images (up to X 300000) than light microscope (up to X10000). But the images will be in black and white because SEM creating images without light waves. SEM is most suitable method to

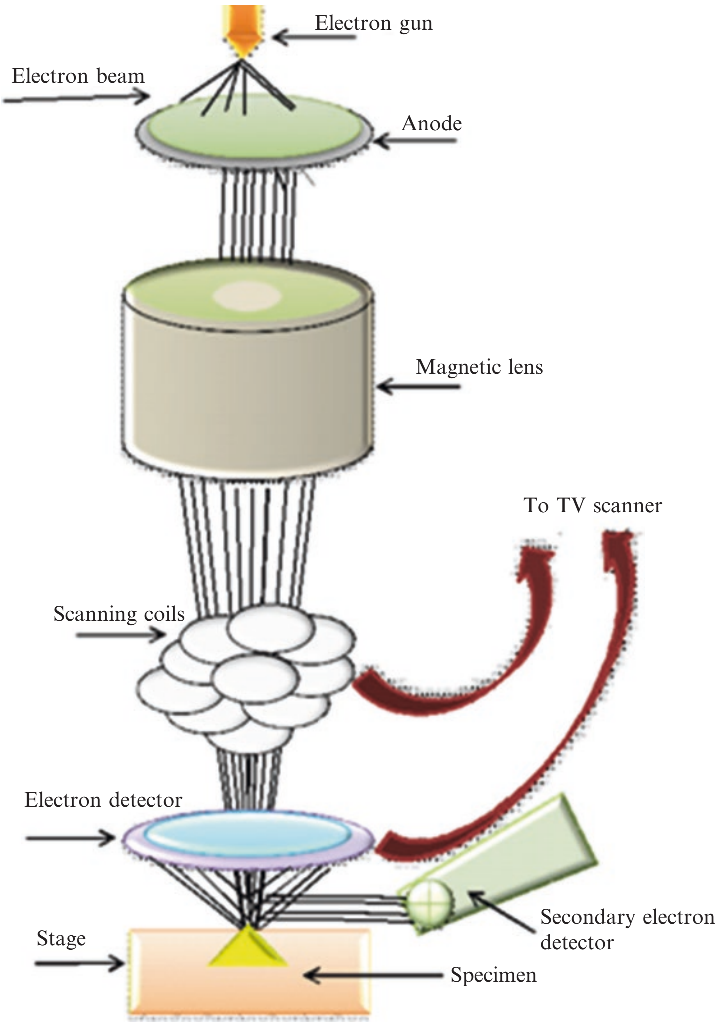


Fig. 4.16 Schematic diagram of SEM

study the nanofibers and nanocoating on polymer. Hence, nanofibers were widely studied in biomedical application, environmental and textile application.

4.4.2 Energy Dispersive X-Ray Analysis

Energy Dispersive X-ray spectroscopy (EDS or EDX) is a technique used for analysis of near surface elements and estimate chemical composition of at different position, thus giving a mapping of the sample.

4.4.2.1 Basic Principle of Energy Dispersive X-Ray Spectroscopy

A beam of electron strikes on the surface of the sample with energy of 10–20 keV which causes to emit X-rays from sample and the energy of the X-ray is depends on the materials under analysis. Images of the each element in the sample obtained by moving the electron beam across the surface of the materials, due to the low intensity of X-rays usually images will generate in number of hours. EDX is a good analysis technique to estimate the composition of the nanoparticles. The gold, silver and palladium nanoparticles compositions can be easily identified whereas elements with low atomic number are difficult to detect by EDX. It is necessary to EDX spectra at different regions of the same materials to get the uniform composition of the bimetallic materials.

4.4.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique to analyze the size, shape and morphology of the material whereby a beam of electrons is transmitted via thin specimen and passes through sample. The formed images from specimen magnified and focused by lens and shows on an imaging screen.

4.4.3.1 Principle of Transmission Electron Microscopy

In the typical TEM, samples will starts to interact with the electron beam by diffraction and this diffraction depends on the orientation of planes of atoms. In the modern TEM instrument, specimen holders that allow the specimen o tilt the specimen at a particular range of angels for diffraction. Hence, high resolution images were obtained by blocking electrons from the microscopy. This produces a difference in the electron intensity that gives information on the crystals. The specimen should be prepared by thin foil to penetrate the electron beam and materials with different dimensions to be electron transparent like nanopowder, nanoparticles and nanotubes etc (Werner et al. 1997).

4.4.4 Atomic Force Microscopy

Atomic force microscopy used for quantitatively measuring the nanometer scale surface hardness or roughness and for displaying the surface nano-texture on many kinds of nanoparticles such as nanocomposites, nanoparticles, nanocoated materials with highly resolution three dimensions of the sample.

4.4.4.1 Basic Principle Atomic Force Microscopy

In atomic force spectroscopy, a probe consisting of a sharp tip in 10 nm size located near the end of cantilever beam was faster scanned on surface of specimen by piezoelectric scanners. The specimen change and interactions were detected using an optical lever monitoring system in which laser can reflected off of the cantilever and on a position sensitive photodiode. While scanning the material operating parameters should be maintain in constant then the imaging of surface of the materials between the optical detection system and the piezoelectric scanners. There are three scanning mode for AFM namely contact mode, non-contact mode and tapping mode. In contact mode, the tip scans the specimen in close contact with materials. The repulsive force on the tip is set by pushing the cantilever against the specimen with piezoelectric scanners. On the other hand, the non-contact mode scans the tip around 50–150 Å. The interaction between the tip and specimen will be measured and generates the images by scanning tip above the surface of materials. In the case of tapping mode, imaging is implemented by moving the cantilever at its resonant frequency using a piezoelectric crystal. When the oscillation of cantilever started with surface of material, oscillation becomes low because of energy loss by the tip contacting the surface and the reduction of oscillation amplitude is used to detect the surface characteristics.

4.4.5 Ultraviolet-Visible Spectroscopy

Ultraviolet visible spectra is consists of a light source, references and sample beams, a monochromator and a detector. Exposing a sample to ultraviolet light from a source light like Xenon lamp a spectrum will obtain at particular visible light range.

4.4.5.1 Basic Principle Behind UV-Vis Spectra

A UV-Visible spectrum is a one type of absorption spectra or reflectance spectra in the ultraviolet region. The absorbance in the visible region affects the color of the sample and undergoes electronic transitions. Absorbance is directly proportional to the path length “b” and the concentration of the sample “c”. Beer’s law states that A=€ bc, where € is Beer’s constant. If several structural groups present in the sample UV spectra shows many absorbance spectrum. When the atoms or molecules absorbs energy, electron are goes to the higher excited state then comes to the ground state by emitting energy. Vibration and rotations are the two modes which present in the atom or molecules that discrete energy levels being on the top of each electronic level. The computer detects that at what wavelength sample will show broad spectrum (Skoog et al. 2007). A schematic representation of UV-Vis spectra shown in Fig. 4.17.

4.4.6 *X-Ray Diffraction (XRD)*

The X-rays are electromagnetic radiation like light but in smaller wavelength and it will produce when electrically charged particles of sufficient energy are decelerated. In X-ray tube electron were drawn on targeted material at high voltage maintained across electrodes.

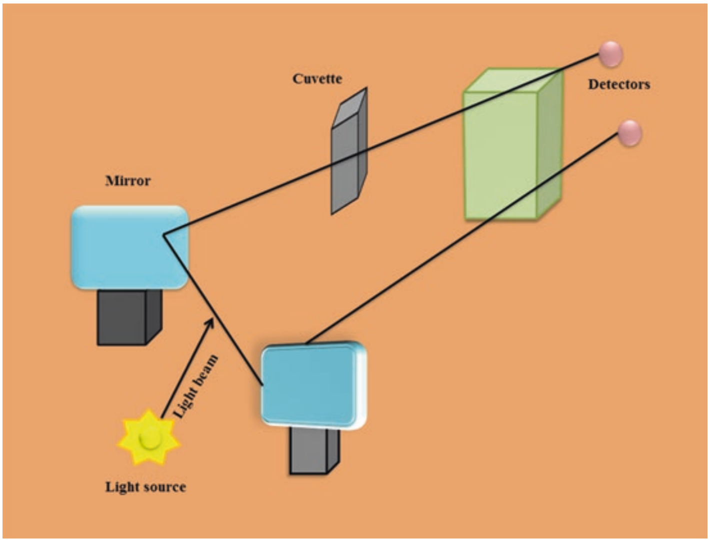


Fig. 4.17 A schematic representation of UV-Vis spectroscopy

4.4.6.1 Basic Principle of X-Ray Diffraction Technique

XRD is technique used to identify the atomic and molecular structures of the materials or crystals, in which atoms causes a beam of incident X-rays to diffract in many directions. By measuring the angles and intensities of the diffracted beam can determine the three dimensional image of the density of electrons. The Bragg's equation used to measure the diffracted angel.

$$2d\sin\varnothing = n\lambda$$

Where, d is spacing between diffracting planes, ϕ is the incident angel, n is any integer and λ represents wavelength of the beam (Bragg 1913).

4.5 Application of Nanomaterials in Agricultural Field

4.5.1 Plant Germination and Growth

Agricultural researchers facing a wide range of problem in crop production, spoil of soil, insect control, low nutrients and water availability. To address all these problems nanotechnology provides many applications. Nanomaterials such as nanoparticles, nanorods, nanosensors etc., were used in agricultural field to detect soil quality and control insect attack. Khodakovskaya and co-workers have reported on the use of carbon nanotubes for improving tomato seed germination. As a result of this study carbon nanotubes has efficiency to provide pores for water availability on seed coat and enhance germination (Khodakovskaya et al. 2009). The nano-fibers like cellulose are a newly developed material used as fertilizer and pesticides. The nano-fibers can also be used as encapsulating chemical pesticides, to prevent scattering of synthetic pesticide in the environment and soil pollution. The nano-fibers easily degrade on the soil and absorb the water insoluble chemical to prevent soil damage. Porous nano-polymers are another important material that can separate organic pollutants from soil and water. Both of the nano-fibers and porous nano-polymers are also used to detect the pathogens (Nicole et al. 2015; Nanditha et al. 2015).

Zheng et al. 2005 have studied nano-TiO_2 and non-nano TiO_2 effect on the growth of spinach seeds (Tables 4.2 and 4.3). The result showed that nano titanium oxide provide enhance growth and 45 % of more chlorophyll in 30 days. Photo- sterilization and photo generation of active oxygen of nano-TiO_2 increased the seed stress resis-

Table 4.2 Metal nanoparticles used for plant growth and germination

Nanoparticle	Size (nm)	Plant name	Concentration	Application
Aluminium	1–100	Radish, rapeseed	2000 mg L^{-1}	Improved root growth
		Ryegrass	2000 mg L^{-1}	Decrease root length
		Corn	2000 mg L^{-1}	Reduced root length
Copper	50	Zucchini	1000 mg L^{-1}	Reduced biomass
		Zucchini	1000 mg L^{-1}	Reduced root growth
Gold	10	Cucumber	100 & 116mg L^{-1}	Positive germination
Silver	10	Wheat	0.5–5.0 mg kg^{-1}	Reduced root length
	5	Barley	10 mg L^{-1}	Reduced germination
	100	Onion	100 mg L^{-1}	Decreased mitosis
Silver colloidal form	0.6–2	Ryegrass	10 mg L^{-1}	Reduced germination
	0.6–2	Ryegrass	20 mg L^{-1}	Reduced germination
	0.6–2	Flax, ryegrass	10 mg L^{-1}	Reduced root length
	0.6–2	Barley, flax, ryegrass	20 mg L^{-1}	Reduced root length
Zinc	0.6–2	Corn, cucumber, lettuce	2000 mg L^{-1}	Reduce root length & elongation
Gold+copper	10	Lettuce	0.013 % (w/w)	Reduced germination

tance and provide capsule penetration for water intake and oxygen. The TiO_2 also increased the inorganic nutrients and reduce the free radicals during photosynthesis process (Zheng et al. 2005). The effect of nanomaterials always may not provide positive results; it also showed negative result on the seed germination process. The nanoparticles of fluorescein isothiocyanate-silica nanoparticles and photostable cadmium selenide quantum dots were applied on rice seed germination. The nanoparticle of fluorescein is othiocyanate-silica was shoed good germination in rice whereas quantum dots arrested the germination (Nair et al. 2011). Lin and Xing have reported on the germination of lettuce, corn and cucumber using carbon nanotubes, aluminium oxide nanoparticles, zinc oxide nanoparticles, aluminium nanoparticles and zinc nanoparticles. All of these materials has significant effect on germination. But, zinc and zinc oxide inhibit the germination while aluminium and aluminium oxide affect the root elongation of corn (Lin and Xing 2007).

4.5.2 Nanoparticles for Pesticide Residue Detection

Nanosensors for pesticide residue detection provide very sensitivity, low detection limits, selectivity, fast response and small size. Some of the nanosensors aimed to detect pesticide residue such as methyl parathion, parathion, fenitrothion, pirimicarb and paraoxon. The carbon, gold, titanium and gold-platinum sensors were used to detect organophosphate, carbamates. Smart nanomaterials can also be used as alternative to sensors for residue detection. The nanomaterials and nanopesticides

Table 4.3 Metal oxide nanoparticles used for plant growth and germination

Nanoparticle	Size (nm)	Plant name	Concentration	Application
Al_2O_3	13	Corn, cucumber	2000 mg L^{-1}	No effect on germination
		Carrot	2000 mg L^{-1}	Decrease root length
		Corn	2000 mg L^{-1}	Reduced root length
CeO_2	7	Alfalfa	1000 mg L^{-1}	Reduced root length
		Tomato	2000 mg L^{-1}	Reduced root growth
FeO	10	Clover	3.2 mg L^{-1}	Reduced biomass
ZnO	8	Soybean	500 mg kg^{-1}	Increased root length
	9–37	Ryegrass	1000 mg L^{-1}	Reduced biomass
	5	Zucchini	1000 mg L^{-1}	Reduced biomass
Fe_3O_4	20	Pumpkin	500 mg L^{-1}	No toxic effect
	7	Cucumber, lettuce	62, 100 mg L^{-1}	Low toxic
		Soybean	20 mg L^{-1}	Increased chlorophyll
TiO_2	5	Spinach	0.25 %	Improved spinach growth
2-amino functionalized SiO_2	8	Lettuce	2000 mg L^{-1}	Improved root growth

act as source of pesticide as well as eliminate the need of sensors for detecting pesticide residue in soil. Nanomaterials have also been studied for degradation of pesticide such as organochlorine pesticide. Yu and co-workers have been studied the degradation of pesticide using nano-TiO_2 film in photocatalytic degradation of organochlorine pesticides. The result was showed that the interaction of peroxide or –OH radical and electron transfer enables the photocatalytic degradation of pesticide on TiO_2 (Yu et al. 2007; Zeng et al. 2010) (Table 4.4).

4.6 Application of Nanomaterial in Food Processing and Packaging

Food processing is the method that converts the raw ingredients into food and other form. Processing includes removal of toxic, prevention of pathogen attack, preservation and improving the consistency of foods for better marketing. Nano capsules delivery systems plays an important role in food processing by encapsulating simple solutions, colloids, emulsions, biopolymers and others into foods. Oxygen is the problematic factor in food processing and packaging that can lead to spoil of food. Nanocomposites with polymer matrix favor the filler matrix interaction and its performance. Nanoclay has been considered as one of the significant composite used in food packaging. The nanoclay or clay based nanocomposites like nylon, polyvinyl alcohol and polylactide are used for polymer matrix in food packaging (John 2010).

Table 4.4 Nanosensors used for pesticide residue detection

Pesticide/herbicide detection	Sensing material	Sensor type
2,4,5 trichlorophenoxy acetic acid	Poly-o-toluidine zirconium (IV) phosphate nanocomposite	Electrochemical
Fenitrothion in water	Nano TiO_2	Electrochemical
Melamine in milk	18-crown-6-ether functionalized gold nanoparticle	Optical
Methyl parathion in water	Nano-ZrO_2/graphite/Paraffin	Electrochemical
Methyl parathion, chlorpyrifos	Nano size polyaniline matrix with SWCNT, single stranded DNA and enzyme	Electrochemical
Parathion in water	Nano-ZrO_2/Au composite	Electrochemical
Parathion in vegetables	Nano-TiO_2 on glassy carbon electrode	Electrochemical

Another important method in food processing and packaging is, to prevent the food from pathogen attack. Generally, silver nanoparticles have capacity to inhibit wide range of biological process (Azeredo 2009). The nanosized powders are mostly used to increase the absorption of nutrients and delivery to cells without affecting color and taste of the food. The nano-fiber, nanoparticles and composites are recently used in the food packaging and this kind of nanomaterials has capacity to undergo biodegradability (Brody 2006) (Table 4.5).

4.7 Conclusion

The opportunity for application of nanoparticle in agricultural and food processing field is prodigious. Nanoparticles, nanosize powder, nanoemulsion and nanocomposites provide a wide range of application in agriculture and food processing. Nanoparticles and nanocomposites as packaging material increase the prevention of pathogen in food and act as oxygen barrier. Biodegradable nanocomposites as packing material are of great potential to environment. Nanosized powder can provide nutritional supply to drug and deliver the drug easily. Application of nanomaterial can help for fast plant germination/production, effective plant protection from environment. Metal and metal oxide nanoparticles have been used as better pesticide to protect crops and nanosensors were utilized to detect pesticide residue in the field. This chapter has also discussed about the synthesis, classification and characterization of nanomaterial as well as application of these nanomaterial in agricultural and food processing industry.

Table 4.5 Few example for food processing and packaging materials

Chain phase	Application	Nanomaterial	Function
Agricultural production	Nanosensors	Nanospray on food commodities hand held devices	Detection of micro-organism
	Pesticide	Nanoemulsion, encapsulates	Increase water solubility
	Water/soil purification	Nanopores	Removal of contaminant
Production and processing of food	Food production	Nano-ceramic devices	Large reactive surface area
	Refrigerators, food preparation equipment, storage container	Zinc and silver nanoparticles	Antibacterial coating
Conservation	Food product	Nano-size silver spray	Antibacterial action
	Packaging material	Incorporated sensors, incorporated nanoparticles, incorporated active nanoparticles	Monitoring food condition, enhance barrier properly, prevent pathogen growth
Functional food, consumption	Additives	Colloidal nanoparticles	Claimed enhance desirable uptake of metal protecting

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Chapter 5
Copper Nanoparticles in Agriculture: Biological Synthesis and Antimicrobial Activity

Ramesh Chand Kasana, Nav Raten Panwar, Ramesh Kumar Kaul, and Praveen Kumar

Abstract Copper is an essential micronutrient incorporated into many proteins and metalloenzymes, and plays a significant role in the health and nutrition of plants. Copper nanoparticles due to unique properties are more efficient than bulk copper particles in activity and functioning. Due to antimicrobial activity copper nanoparticles are finding new applications in agriculture, healthcare and industry. However there are growing concerns regarding the indiscriminate use of either copper or copper nanoparticles which can cause toxic effects to plants and other living organisms. We review here the biological synthesis of copper nanoparticle using plant extracts and microorganisms; antibacterial and antifungal activity of copper nanoparticles and the impact of copper nanoparticles on crops and pathogenic microorganisms.

Copper nanoparticles of various sizes ranging from 5 to 280 nm have been synthesized by using extracts prepared from *Syzygium aromaticum*, *Tabernaemontana divaricate*, *Vitis vinifera*, *Aloe vera*, *Cassia alata*, *Centella asitica*, *Bifurcaria bifurcate*, *Gloriosa superba* and *Citrus medica*. Biosynthesis of small spherical copper oxide nanoparticles ranging from 5 to 10 nm or with average size of 15 nm have been achieved by using leaf extract or latex produced by plants. Copper nanoparticles ranging from 5 to 295 nm have also been synthesized by using microorganisms both bacteria and fungi. Comparisons of microbial synthesized copper nanoparticles with those synthesized using plant extracts have shown that those synthesized by microorganisms had smaller dimension. Copper nanoparticles ranging in size from

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5 to 50 nm were synthesized in about 80 % sample of microorganisms and about 70 % samples of plant extracts screened for synthesis.

Biologically-synthesized copper nanoparticles show good antibacterial and antifungal activity inhibiting the growth of pathogenic bacteria belonging to Gram positive and Gram negative genera, and plant pathogenic fungi. Growth inhibition has been seen in case *Staphylococcus aureus*, *Enterococcus faecalis*, *Propionibacterium acnes*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, *Shigella flexneri*, *Proteus vulgaris* and *Salmonella typhimurium*. Antifungal activity of copper nanoparticles against the pathogenic fungi *Fusarium culmorum*, *Fusarium oxysporum*, *Fusarium graminearum* and *Phytophthora infestans* has also been recorded. Copper nanoparticles at concentrations below 100 ppm have been reported to enhance germination and growth of some plants.

Keywords Copper • Nanoparticles • Agriculture • Crops • Soil • Microorganisms • Pathogen • Biosynthesis • Plant • Antimicrobial

5.1 Introduction

The agriculture and healthcare sectors have witnessed great strides during last few decades. However due to ever increasing population many developing countries still face the threat of food/healthcare insecurity (Husen and Siddiqi 2014). The synthesis of nanoparticles and recent innovations in nanobiotechnology has opened new avenues for their exploitation in both of these sectors. In healthcare increased resistance of microorganisms to drugs has forced researchers to develop alternative antimicrobial agents including cationic polymers, metal nanoparticles and antimicrobial peptides (Ren et al. 2009; Ahamed et al. 2014). In agriculture, nanotechnology has found wider applications in post-harvest storage of food products but its application in improving crop productivity is recent one. Attention is now being paid to increase crop productivity by enhancing plant growth and reducing the impact of abiotic and biotic stresses through nano-technological interventions.

Copper is an essential micronutrient whi ch plays important role to the health of all living organisms. Copper is incorporated into an array of proteins and metalloenzymes required for performing various metabolic functions by the plant cells/organisms. Copper has an outstanding electrical conductivity, good catalytic behavior and surface enhanced Raman scattering activity, and hence copper nanoparticles have attracted the attention of researches for using it as an essential component in the future nano-devices (Chandra et al. 2014). Nanoparticles of copper have also gained importance due to their wide spread applications as antimicrobials, in gas sensors, electronics and coating on textiles, batteries, solar energy conversion tools and high temperature superconductors (Chen et al. 2012). Copper nanoparticles effectively inhibit growth of many pathogenic bacteria like *Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Shigella dysenteriae, Salmonella typhi, Klebsiella* *pneumoniae*, (Cioffi et al. 2005; Abboud et al. 2014; Ahamed et al. 2014; Sutradhar et al. 2014; Naika et al. 2015) and possess good antifungal activity against various pathogenic fungi (Kanhed et al. 2014; Shende et al. 2015). Copper nanoparticles have also found applications in eco-toxicological assay due to comparatively low dissolution and high toxicity against macro/microorganisms (Buffet et al. 2011).

In spite of enormous beneficial uses of nanoparticles in general and copper in particular, the fate and impact of these nanoparticles in environment is a matter of concern (Schilling et al. 2010; Song et al. 2015). The potential risks associated with production, application and disposal of nanoparticles especially copper nanoparticles therefore need to be investigated before releasing them into public domain.

5.2 Biosynthesis of Copper Nanoparticles Using Plant Extracts

Nanoparticles of copper have been synthesized from various salts of copper like copper acetate, copper chloride, copper sulphate and copper nitrate using extracts made from various plants belonging to different groups. Although copper nanoparticles have been synthesized by physical and chemical methods for quite some time now, the biological synthesis of copper nanoparticles has started recently. Copper nanoparticles with average size of 15 nm were synthesized by addition of 20 ml of *Calotropis procera* L. latex solution to 20 ml 3.0 mM aqueous copper acetate solution at room temperature with continuous shaking (Harne et al. 2012). Synthesis of copper nanoparticles ranging from 5–40 nm by *Syzygium aromaticum* was carried out using *Syzygium aromaticum* aqueous extract and 0.001 M copper sulphate in 1:1 ratio (Subhankari and Nayak 2013). Mono dispersed copper oxide nanoparticles of 46 nm size were synthesized by using *Tabernaemontana divaricate* leaf extract and mixing copper sulphate to it under constant stirring (Sivaraj et al. 2014). *Vitis vinifera* leaf extract 10 ml was added into 40 ml aqueous solution of 1 mM copper sulphate in test tube and kept for incubation in darkroom at room temperature for synthesis of nanoparticles of copper (Angrasan and Subbaiya 2014).

The synthesis of copper oxide nanoparticles ranging in size from 110–280 nm was carried out by adding heated 1.0 mM copper sulphate solution to the heated aqueous extract of flowers of *Cassia alata* at 1:1 ratio and stirring with glass rod for 10 min and again heating at 80 °C for 45 min (Jayalakshmi and Yogamoorthi 2014). Copper nitrate and either tea leaf extract or coffee powder extract were taken in 1:3 ratio and the solution was subjected to microwave heating at 540 W for 7–8 min producing copper oxide nanoparticles with a size of 50–100 nm (Sutradhar et al. 2014). In another study addition of 10 ml of *Centella asiatica* leaves extract to 100 ml of 1 % copper acetate and continuous stirring for about 3 h resulted in the formation of copper nanoparticles with average diameter in range of 2–5 μm (Devi and Singh 2014). The addition of 2 ml brown alga *Bifurcaria bifurcata* extract drop wise into 20 ml of 1 mM aqueous solution of copper sulfate with constant stirring at

100–120 ºC resulted in the biosynthesis of copper oxide nanoparticles ranging from 5 to 45 nm (Abboud et al. 2014). Filtered extract of fruit juice of *Citrus medica* Linn was added to 100 mM copper sulphate solution and the solution was mixed thoroughly, poured into an aluminium vessel for the reaction and gradually heated to boiling at 60–100 °C to obtain copper nanoparticles in the range of 10–60 nm with an average size of 33 nm (Shende et al. 2015). In another study, copper nanoparticles were synthesized by adding 20 ml of flowers broth of *Aloe vera* to 20 ml of 5 mM copper acetate aqueous solution in the dark and the reaction was performed at 50 ºC in a steam bath for 30 min resulting in spherical nanoparticles of copper with average size was 40 nm (Karimi and Mohsenzadeh 2015). For synthesis of copper nanoparticles the reaction mixture was prepared by adding 1 ml of the *Gloriosa superba* L. extract and 2.32 g cupric nitrate as a source of copper. Small amount of double distilled water was added to get homogenous mixture under constant stirring for 10 min. This reaction mixture was kept in a pre-heated muffle furnace maintained at 400 °C for 3–4 min leading to synthesis of spherical copper oxide nanoparticles having size in the range 5–10 nm (Naika et al. 2015).

In another study for the synthesis of copper nanoparticles *Citrus medica* fruit extract was added to 1 mM solution of copper sulphate in the ratio 1:10 and shaken vigorously for proper mixing of reactants followed by heating in aluminum vessel at 50 °C for 15 min. Nanoparticles within the range of 17–93 nm with an average size of 54 nm were formed (Nagaonkar et al. 2015). Thoroughly washed 5 gram fresh Andean blackberry fruit and 5 gram leaves were heated at 65–70 °C in 50 ml of deionized water for 60 min and, 0.3, 0.5, 1.0 and 1.5 ml of filtrate was mixed with 10 ml of 10 mM copper nitrate solution and stirred for 6 h at 75–80 °C for synthesis of copper oxide nanoparticles with mean diameter of 43.3 nm and 52.5 nm using Andean blackberry fruit and leaf extract respectively (Kumar et al. 2015). From the above review it is clear that nano particles of varying size can be synthesized by using various plant extracts and different salts of copper.

5.3 Microbial Synthesis of Copper Nanoparticles

In case of microbial synthesis of nanoparticles different strategies are employed viz (i) growing microorganisms can be used for synthesis of nanoparticles (ii) the extracellular secretion from microorganisms can be used for synthesis of nanoparticles and (iii) the biomass from living and dead microorganism can be used for synthesis of nanoparticles. General methods for synthesis of copper nanoparticles using microorganisms are shown in Fig. 5.1. Research on synthesis of nanoparticles of copper using bacteria and fungi had started in last decade only and there is scarce information on the subject. In the first paper on microbial synthesis of copper nanoparticles, a Gram negative bacterium belonging to the genus *Serratia*, isolated from the mid gut of *Stibara* species, an insect produced polydispersed nanoparticles of copper varying from 10–30 nm in diameter using different concentrations of copper sulphate with 5 mM as the best concentration (Hasan et al. 2008). *Pseudomonas*

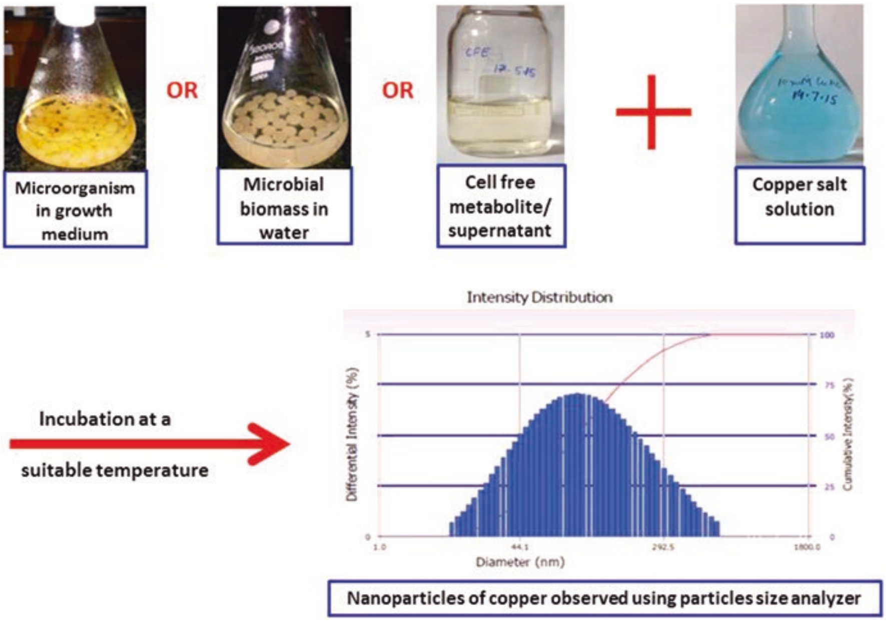

Fig. 5.1 Microbial synthesis of copper nanoparticles is carried out by one of these methods (i) to microorganisms growing in growth medium copper salt is added (ii) to microbial biomass taken in water copper salt is added (iii) to extracellular secretion from microorganisms copper salt is added. Then incubation is done at a suitable temperature. Synthesized nanoparticles as observed using particles size analyzer

stutzeri isolated from soil was used for synthesis of copper nanoparticles by using 1 mM copper sulphate and spherical copper nanoparticles of 8–15 nm produced (Varshney et al. 2010). Extracellular synthesis of copper oxide nanoparticles using 1 mM copper sulphate and *Escherichia coli* resulted in Quasi-spherical nanoparticles ranging in size from 10–40 nm (Singh et al. 2010).

Aqueous phase biosynthesis of metallic copper nanoparticles of quasi-spherical morphology ranging in diameter from 15–20 nm, with an average particle diameter of 19.2 nm was carried out using a silver resistant bacterium *Morganella morganii* and 5 mM copper sulphate solution (Ramanathan et al. 2013). Three fungi *Penicillium aurantiogriseum, Penicillium citrinum* and *Penicillium waksmanii* isolated from soil were used for synthesizing and stabilizing copper nanoparticles. Three different concentrations of copper sulphate viz. 1 mM, 3 mM and 5 mM and five pH: 5, 6, 7, 8 and 9 were used for extracellular synthesis of copper nanoparticles ranging from 79–295 nm under different conditions (Honary et al. 2012). Biosynthesis of copper nanoparticles using dead biomass of *Hypocrea lixii* and copper chloride resulted in the formation of spherical shape copper nanoparticles with an average diameter of 24.5 nm (Salvadori et al. 2013).

In another study extracellular production of spherical copper nanoparticles of 87.5 nm was carried out by using dead biomass of *Trichoderma koningiopsis*

(Salvadori et al. 2014). Spherical and hexagonal copper nanoparticle of 49 nm were synthesized by using 10 ml cell-free culture supernatant of non-pathogenic bacterium *Pseudomonas fluorescens* MTCC103 and 40 ml of 318, 750 and 1000 ppm copper sulphate solutions (Shantkriti and Rani 2014). Extracellular biosynthesis of copper nanoparticles using cell free supernatants of *Salmonella typhimurium* and 1 mM copper nitrate gave nanoparticles with average size of 49 nm (Ghorbani et al. 2015). *Stereum hirsutum*, a fungus from Southern Chilean forests was used for biosynthesis of copper/copper oxide nanoparticles ranging from 5–20 nm using three different copper salts, copper chloride, copper sulphate and copper nitrate at final concentration of 5 mM (Cuevas et al. 2015). An overview of concentration of salts, microorganisms and biosynthesis conditions is given in the Table 5.1.

From the above discussion it is clear that copper nanoparticles of different shape and size have been synthesized by using plant extracts from various genera as well as by using various microorganisms; both fungi and bacteria. Though the nanoparticles can be produced using extracts from various plants the more emphasis should be given to the microbial synthesis because commercial biosynthesis using plant extracts is not a viable strategy due to requirement of large amount of raw material. As microorganisms can be grown and multiplied under the lab conditions, moreover they can be manipulated and operated for optimal production of nanoparticles, so microorganisms will be more suitable for commercial production of copper nanoparticles.

5.4 Antimicrobial Activity of Copper Nanoparticles

Various studies have suggested that copper nanoparticles can be used as antimicrobial or/ antibacterial agents. The antimicrobial activities of copper nanoparticles have been reported against an array of plant and human pathogenic bacteria and fungi belonging to various genera and species. This section deals with the antimicrobial activity studies carried out with the copper nanoparticles.

The copper nanoparticles synthesized using tea leaf or coffee powder extract showed antibacterial activity against human pathogenic microbes viz., *Shigella dysenteriae* 1, *Vibrio cholerae* non.0139 (L4), *Vibrio cholerae* non.0139 (CSK6669), *Streptococcus pneumoniae*, *Staphylococcus aureus* and *Escherichia coli* (Sutradhar et al. 2014). The antibacterial activity of copper nanoparticles synthesized using brown alga *Bifurcaria bifurcata* extract showed radial diameter of the inhibition zone of *Enterobacter aerogenes* and *Staphylococcus aureus* as 14 and 16 mm, respectively (Abboud et al. 2014). Copper oxide nanoparticles synthesized by *Tabernaemontana divaricate* leaf extract showed maximum zone of inhibition at concentration of 50 μg/ml copper oxide nanoparticles against urinary tract pathogen *Escherichia coli* (Sivaraj et al. 2014). Copper nanoparticles synthesized using *Vitis vinifera* leaf extract showed a clear zone of growth inhibition against *Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae, Salmonella typhi* and *Bacillus*

Table 5.1 Synthesis and characterization of copper nanoparticles by microorganisms

S. No.	Microorganism	Salt and concentration	Synthesis conditions	Particle shape and size	Characterization methods	References
1	*Morganella morganii*	5 mM $CuSO_4$	Grew in Luria Bertani broth without NaCl at 37 °C for 24 h. Added 5 mM equivalent of $CuSO_4$. Incubated for up to 20 h at 37 °C under shaking.	Quasi-spherical 19.2 nm	UV-visible absorbance spectroscopy, transmission electron microscopy (TEM) and high resolution TEM (HR-TEM), X-ray photoemission spectroscopy (XPS)	Ramanathan et al. (2013)
2	*Serratia*	1,3, 5, 7 and 10 mM $CuSO_4$	Grew in Luria Bertani broth medium, at 37 °C, 220 rpm for 24 h. The pellet was suspended in distilled water and $CuSO_4$. The culture was incubated for another 48 h at 37 °C and 220 rpm	10–30 nm	UV-visible absorbance spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS) and fourier transform infrared spectroscopy (FTIR)	Hasan et al. (2008)
3	*Pseudomonas fluorescens*	318, 750, 1000 ppm $CuSO_4$	Grew in King's B medium at 30 °C in an incubator shaker set at 150 rpm. 1 gram of biomass was suspended independently in 20 ml of 318, 750 and 1000 ppm ($CuSO_4$) solution. Different volumes of cell-free supernatant added to various concentrations of CuSO4 solution and incubated in shaker for 24–48 h at 30 °C, 150 rpm.	Spherical and hexagonal 49 nm	UV-visible spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDS), transmission electron microscopy (TEM) and selected area electron diffraction (SAED)	Shantkriti and Rani (2014)

(continued)

Table 5.1 (continued)

S. No.	Microorganism	Salt and concentration	Synthesis conditions	Particle shape and size	Characterization methods	References
4	*Trichoderma koningiopsis*	100 mg/l $CuSO_4$	Grew in Sabouraud broth at 25 °C for 5 days, under shaking at 150 rpm, pellets harvested and washed and for the preparation of dead biomass, live biomass was autoclaved and dried at 50 °C and ground to obtain uniformly sized particles	Spherical 87.5 nm	Scanning electron microscopy (SEM), energy dispersive X-ray (EDS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy(XPS)	Salvadori et al. (2014)
5	*Hypocrea lixii*	100 mg/l $CuCl_2$	Grew in Sabouraud broth at 25 °C for 5 days, under shaking at 150 rpm, pellets harvested and washed and for the preparation of dead biomass, live biomass was autoclaved and dried at 50 °C and ground to obtain uniformly sized particles	Spherical 24.5 nm	Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) X-ray diffraction (XRD) fourier transform infrared spectroscopy (FTIR)	Salvadori et al. (2013)
6	*Pseudomonas stutzeri*	1 mM $CuSO_4$	Grew in nutrient broth at 37 °C for 24 h and pellet was suspended carefully weighted 0.1 g biomass was added to 100 ml of 1 mM aqueous $CuSO_4$ solution, incubated in incubator shaker at 150 rpm at room temperature	Spherical 8–15 nm	UV-visible spectroscopy, x-ray diffraction, and high resolution transmission electron microscopy (HR-TEM).	Varshney et al. (2010)
7	*Penicillium aurantiogriseum, P. citrinum, P. waksmanii*	1, 3 and 5 mM $CuSO_4$	Grew on Czapek dox broth at 28 °C and 200 rpm for 10 days. Centrifuge and take the supernatant. Added 100 ml of $CuSO_4$ solution to 100 ml of supernatants	Spherical 79–295 nm	Scanning electron microscopy (SEM), dynamic light scattering (DLS), UV-visible and fluorescence spectrum	Honary et al. (2012)

8	*Escherichia coli*	1 mM $CuSO_4$	Grew bacterium in 100 ml of citrate minimal medium for 15 h at 150 rpm at 28 °C. Then 30 grams of bacterial biomass was washed thrice under sterile conditions and resuspended in 100 ml of 10^{-3} M aqueous $CuSO_4$ solution and further incubated at 150 rpm for 42 h at 28 °C	Quasi-spherical 10–40 nm	UV-Vis-spectrophotometry, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) pattern, fourier transform infrared (FTIR) spectroscopy	Singh et al. (2010)
9	*Stereum hirsutum*	5 mM $CuCl_2$, $Cu(NO_3)_2$ and $CuSO_4$,	Grew in 100 ml medium (pH 5.0) containing 15 g/ L glucose, 5 g/ L potato peptone, and 2.5 g/L yeast extract for 15 days at 100 rpm and 25 ∘C. Then 8 g of fungal biomass was transferred into 50 ml of sterilized deionized water and incubated in shaker at 100 rpm for 24 h at 25 °C. To 50 ml of mycelium free extract $CuCl_2$, $Cu(NO_3)_2$, and $CuSO_4$, were added to make final concentration of 5 mM. Incubated at 25 °C and 100 rpm for 7 days	Spherical 5–20 nm	UV-visible spectroscopy, transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), and fourier transforms infrared spectroscopy (FTIR)	Cuevas et al. (2015)
10	*Salmonella typhimurium*	1 mM $Cu(NO_3)_2$	Grew in Muller- Hinton broth. Centrifuged at 5000 for 20 min. The supernatant was added to copper nitrate at a concentration of 1 mM. The reaction was carried out for 40 min	49 nm	UV-visible spectroscopy, dynamic light scattering (DLS), and scanning electron microscopy (SEM)	Ghorbani et al. (2015)

subtilis confirming the antibacterial property of biologically synthesized nanoparticles (Angrasan and Subbaiya 2014).

In vitro antifungal activity of chemically synthesized copper nanoparticles was carried out against four different plant pathogenic fungi *Phoma destructiva* DBT66, *Curvularia lunata* MTCC 2030, *Alternaria alternata* MTCC 6572 and *Fusarium oxysporum* MTCC 1755 using disc diffusion method. Copper nanoparticles showed remarkable activity against all the mentioned plant pathogenic fungi with maximum antifungal activity against *Curvularia lunata* MTCC 2030 followed by *Alternaria alternata* MTCC 6572 and minimum activity against *Phoma destructive* DBT 66 (Kanhed et al. 2014). Antimicrobial activity of copper oxide nanoparticles synthesized by precipitation technique was analyzed against various bacterial strains *Escherichia coli*, *Pseudomonas aeruginosa, Klebsiella pneumoniae, Enterococcus faecalis, Shigella flexneri, Salmonella typhimurium, Proteus vulgaris*, and *Staphylococcus aureus* using a well diffusion assay. It was reported that copper oxide nanoparticles demonstrated excellent antimicrobial activity against these bacteria with *Escherichia coli* and *Enterococcus faecalis* exhibiting the highest sensitivity toward copper oxide nanoparticles while *Klebsiella pneumoniae* showed the least sensitivity among the tested microorganisms (Ahamed et al. 2014). Antimicrobial studies on nanoparticles synthesized by *Gloriosa superba* L. carried out by agar well diffusion method showed that nanoparticles exhibit significant antibacterial activity against pathogenic bacterial strains namely *Klebsiella aerogenes*, *Pseudomonas desmolyticum*, *Escherichia coli* and *Staphylococcus aureus* (Naika et al. 2015). It was reported that the copper nanoparticles synthesized using Citron juice from *Citrus medica* Linn. demonstrated a significant inhibitory activity against *Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa, Propionibacterium acnes* and *Salmonella typhi* as well as against plant pathogenic fungi, *Fusarium culmorum, Fusarium oxysporum* and *Fusarium graminearum* (Shende et al. 2015).

Cytotoxicity of *Calotropis procera* L. latex synthesized and stabilized copper nanoparticles on HeLa, A549 and BHK21 cell lines was assessed by 3-(4, 5-dimethylthiazole-2-yl)-2, 5-diphenyl tetrazolium bromide dye conversion method and it was reported that after 24 h treatment with filter sterilized copper nanoparticles on HeLa, A549 and BHK21 cell lines showed excellent viability even up to 120 μM concentrations of copper nanoparticles (Harne et al. 2012).

Keeping in mind the above finding that the copper nanoparticles showed good antimicrobial activity against the pathogenic bacteria belonging to Gram positive and Gram negative genera, and plant pathogenic fungi suggest their use as antimicrobial agent. Copper nanoparticles with antimicrobial activity can be employed for the production of a broad range of polymer nanocomposites. These polymer/copper nanocomposites can be used in the preparation of antibacterial paints/coatings for application in household, biomedical and aerospace industries. Furthermore copper nanoparticles embedded into polymer matrix can be employed in the food-packaging field for delay of deterioration, shelf life extension, maintaining quality and safety of packaged food.

5.5 Impact of Copper Nanoparticle on Agriculture Crops and Soil Microorganisms

Metal- and metal oxide-based nanomaterials have been shown to act as mediators of DNA damage in mammalian cells, organisms and even in bacteria, but the molecular mechanisms through which this occurs are poorly understood (Atha et al. 2012). The effect of copper nanoparticles at different concentrations starting from 0, 200, 400, 600, 800 to 1000 mg/l on the growth of plant seedling of the plant species *Phaseolus radiates* and *Triticum aestivum* showed that seedling lengths of test species were negatively related to the exposure concentration of copper nanoparticles (Lee et al. 2008). The effect of copper oxide-nanoparticles of <50 nm size on germination and growth of seeds of *Glycine max* L. and *Cicer arietinum* L. showed that in both the crops, germination occurred up to 2000 ppm copper applied through copper oxide-nanoparticles, but the root growth was prevented above 500 ppm copper (Adhikari et al. 2012). Plant growth inhibition for *Raphanus sativus*, perennial *Lolium perenne* and annual *Lolium rigidum* was reported on treatment with copper oxide nanoparticle under controlled laboratory conditions. The growth inhibition probably was due to substantial buildup of oxidatively modified, mutagenic DNA lesions like 7,8-dihydro-8-oxoguanine; 2,6-diamino-4-hydroxy-5-formamidopyrimidine; 4,6-diamino-5-formamidopyrimidine (Atha et al. 2012). Studies conducted on effect of copper oxide nanoparticles in *Glycine max* L. showed that exposure to 500 mg/l of copper oxide nanoparticles significantly reduced the shoot growth, weight and total chlorophyll content. Whereas, the root length and fresh weights were significantly reduced at all the concentrations of copper oxide nanoparticles exposure; 50, 100, 200, 400, and 500 mg/l (Nair et al. 2014a).

The effect of copper oxide nanoparticles at different concentrations 0, 0.5, 1, 2, 5, 10, 20, 50, and 100 mg/l on *Arabidopsis thaliana* showed that there was significant reduction in plant biomass and total chlorophyll content on exposure to 2, 5, 10, 20, 50, and 100 mg/l copper oxide nanoparticles. However there was increase in anthocyanin content at 10, 20, 50 and 100 mg/l, lipid peroxidation at 5, 10, and 20 mg/l and amino acid proline content at 10 and 20 mg/l concentrations of copper oxide nanoparticles (Nair et al. 2014b). Exposure of *Spirodela polyrhiza*, *Lemna minor* and *Wolffia arrhiza* to 25 nm spherical copper nanoparticles showed that frond area based relative growth rate was the most sensitive endpoint, with an EC_{50} (concentration of a compound where 50 % of its maximal effect is observed) of 1.15 mg/l for *S. polyrhiza*, 0.84 mg/l for *L. minor* and 0.64 mg/l for *W. arrhiza* (Song et al. 2015).

The studies conducted on effect of copper nanoparticles on actively dividing cells of mitosis in *Allium cepa* revealed that copper nanoparticles increased mitotic index up to the concentration of 20 μg/ml, and a gradual decline in mitotic index and increase in abnormality index was observed as the concentration of copper nanoparticles and treatment duration were increased. Aberrations in chromosomal behavior were also reported (Nagaonkar et al. 2015).

The impact of copper and zinc oxide nanoparticles on the soil microbial community measured using culture-dependent and culture-independent methods showed that nanoparticles altered the microbial community structure. Particularly microorganisms belonging to two orders Flavobacteriales and Sphingomonadales found in rhizosphere, appeared to be mainly susceptible to the presence of nanoparticles (Collins et al. 2012). Twenty-one bacterial strains isolated from agricultural soil were used to evaluate the cytotoxicity of copper oxide nanoparticles and strains like *Brevibacillus laterosporus*, *Chryseobacterium indoltheticum* and *Pantoea ananatis* showed high sensitivity (Guerrero et al. 2014). When aquatic macrophyte *Lemna gibba* L. plants were exposed to copper oxide nanoparticles or soluble copper, inhibition of photosynthetic activity was found as indicated by the inactivation of Photosystem II reaction centers, a decrease in electron transport and an increase of thermal energy dissipation (Perreault et al. 2014). From the review of literature on impact of copper nanoparticle on plants it is clear that barring few examples copper nanoparticles do not have much effect on germination and growth of plants. However studies on effect of copper nanoparticles gains importance for exploring the nanoparticles for diseases management without impacting the plant growth.

5.6 Copper Nanoparticles in Disease Management

As discussed in the earlier part of this article the copper nanoparticles have shown antimicrobial activity against broad range of pathogenic bacteria and fungi resulting in creating interest for evaluating nanoparticles for disease control in agriculture, where fungi and bacteria cause damages to many crops. Copper based fungicide play an important role in disease prevention and treatment in a variety of plant species (Borkow and Gabbay 2005). Three different copper based nanoparticles of similar sizes i.e. 11–14 nm and shapes, Cu_2O, CuO and Cu/Cu_2O respectively, were tested in the field against *Phytophthora infestans* on *Lycopersicon esculentum* (tomato) under protected cultivation. The results showed that all the tested copper based nanoparticles were more effective in lower formulated product and active ingredient rate than the four registered copper based agrochemicals. Along with the promising efficacy, it was also found that copper-based nanoparticles did not induce any permanent damage/deleterious effect to the plants (Giannousi et al. 2013). In case of use of copper nanoparticles in disease management it is the beginning which will have to go long way for protecting the various plants from diseases in sustainable manner.

5.7 Conclusion

Copper nanoparticles are among one of the important nano materials due to their diverse properties and applications. Copper nanoparticles can be synthesized by physical and chemical methods, but in recent past biological methods are being preferred due to the ease and environmental concerns. The biologically synthesized copper nanoparticles have shown some promising result against pathogens, but their application in field is yet in very preliminary stages. For exploiting the benefits of biologically synthesized nanoparticles thorough studies on the doses required for plant growth and disease control need to be carried out in various crops.

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Chapter 6
Nanoparticles to Sense Food Quality

Vineet Kumar, Praveen Guleria, and Surinder Kumar Mehta

Abstract Food contains various nutritionally constituents for animal and human growth. Food material also supports the growth of microorganisms. Microorganisms can cause infection or produce toxins that adversely affect human health. Further, food adulteration and brand protection is also a serious problem. Therefore food processing, storage and transport can lead to risk of food contamination, adulteration and degradation of sensitive food ingredients.

We review here the application of nanomaterials for food quality sensing. Organic and inorganic nanoparticles have application in detection of disease causing microorganism, toxic chemicals, food freshness, product authenticity, brand protection, and artificial smell and taste sensing. Nanosensors can sense pathogenic bacteria in food items with single cell level sensitivity. Nanoparticles are also successfully used for the detection of food-contaminating toxins, namely aflatoxin, palytoxin, Botulinium neurotoxin, ochratoxin, zearalenone and HT-2. Nanoparticles are also used for the detection of toxic contaminants such as dyes, fertilizer and pesticides in food. These applications are further widened to vitamins, essential amino acid and hydrogen peroxide. Nanoparticles functionalized with biological receptors can also sense odorant and tastant with human-like efficiency.

Keywords Nanoparticles • Food • Microorganism • Sensing • Toxin • Brand protection

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6.1 Introduction

Food is the primary and fundamental need of humans. Food safety is a global concern. Microorganism causes several diseases in humans. Microorganisms also generate toxins as defensive agents that are very harmful to humans. Food contaminated with such microbes or toxins can cause human health problems ranging from vomiting, diarrhea to paralysis and even death. Food adulteration is another serious problem. The problem is even worse in case of warfare i.e. use of such toxins or chemicals in water, food or air. So, there is a need to develop easy, cost-effective and sensitive detection approaches against harmful chemicals, bacteria and related toxins (Franz et al. 1997; Leggiadro 2000; Zhu et al. 2009). In this context, nanotechnology applications in food and nutraceutical industry is vastly emerging (Fig. 6.1). Nanomaterials, popularly known as nanoparticles have unique properties due to their small size and large surface area.

Nanoparticles are also being explored for the development of cost-effective and fast detection techniques for sensing contamination, adulteration and freshness of food materials. Nanoparticle based sensors have emerged as easy and sensitive detection techniques for the food industry (Farahi et al. 2012; Kara et al. 2013). Food products have high nutritional value that lead to their easy microbial contamination. Further, the food products contain constituents that may degrade in time and/or in a temperature dependent manner. So, packaging of food products is important for their global commercial viability. Traditional passive packaging systems are not sufficient due to the recent threat of food bioterrorism and increased concern for

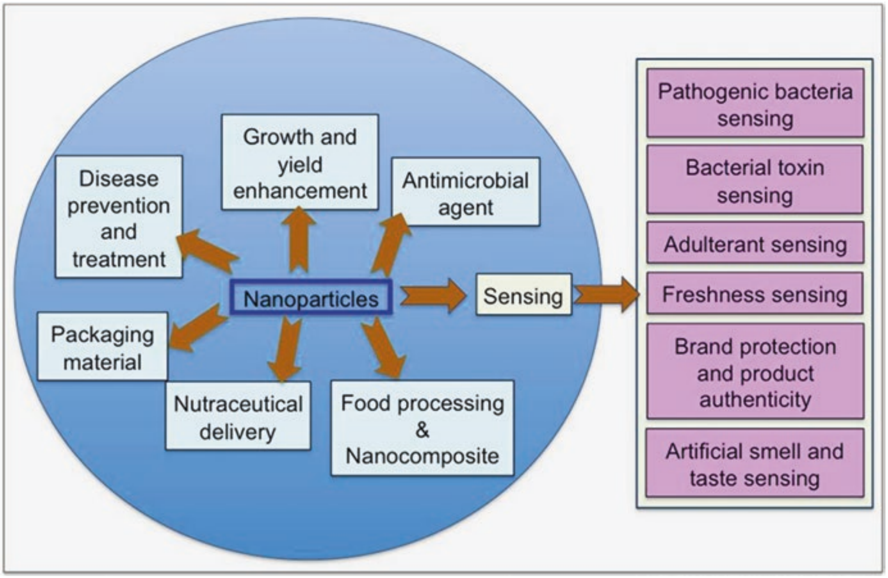

Fig. 6.1 Diagram showing various applications of nanoparticles in food industry

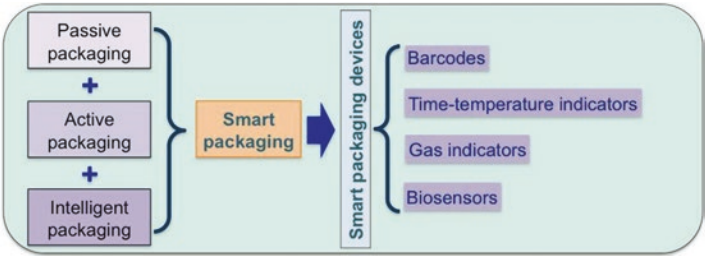

Fig. 6.2 Schematic diagram showing various smart packaging devices

food safety. Active packaging was opted as its alternate, which was taken over by intelligent packaging. Intelligent packing has, thus emerged as better alternate to traditional packaging that acts as passive barrier against dust, air and moisture (Kuhn 1996; Yam et al. 2005). Active packaging involves interaction of packaging material with food and environment to enhance the shelf life of food items (Vermeiren et al. 1999). Whereas intelligent packaging can detect, sense, record, trace, communicate and apply scientific logic to identify and protect the shelf life, brand name and quality of packed food. Sensing is an important part of intelligent packaging system (Yam et al. 2005). Intelligent packaging uses various smart packaging devices like barcodes, time-temperature indicators, gas indicators and biosensors (Fig. 6.2). They also have a key role to play as new and next generation smart nano-packaging materials in food industry.

Protection of tags for authenticating the originality of food products is also important. Existing barcodes are very easy to manipulate. So, nanoparticles are being used for developing cost-effective, invisible and sophisticated tags that could verify the originality of food products. Nanoparticles based invisible nanobarcodes also have the potential to revolutionize the brand protection industry (Banu et al. 2006; Birtwell et al. 2008). The sensing applications of nanoparticles in the field of food and nutrition have been reviewed in the present article (Fig. 6.1).

6.2 Nanoparticle Based Sensors for Detection of Food Contaminating Microorganisms, Toxins and Adulterants

The food items are good to consume only if they are fresh and free from adulterants and contaminants. Food contaminated with microbes and toxic chemicals can cause serious health problems. Various regulatory guidelines have been formulated to maintain the quality of food. But the detection of adulteration and contaminants in foodstuffs at low level is quite tedious. Nanoparticles based sensors has been successfully employed to detect the toxic chemicals and microorganisms with high sensitivity (Table 6.1).

Table 6.1 Nanoparticles based detection of food pathogenic bacteria

Type of nanoparticle	Method/technique	Microorganism	References
Zinc sulphite-cadmium selenide	Fluorescence microscopy	*Escherichia coli*, *Salmonella typhimurium*	Su and Li (2004), Yang and Li (2006), and Liu et al. (2008)
Tris-(2,2-bipyridyl) dichlororuthenium(II) hexahydrate doped silica	Spectrofluorometry and flow cytometry	*E. coli, S. typhimurium* and *B. cereus*	Zhao et al. (2004)
Iron oxide	Bioluminescence, Interdigitated array microelectrode-based impedance analysis, polymerase chain reaction and spectrofluorometry	*E. coli*, *L. monocytogenes* and *S. typhimurium*	Amagliani et al. (2004), Varshney et al. (2007), Varshney and Li (2007), Yang et al. (2007), Cheng et al. (2009), Ravindranath et al. (2009), and Zhou et al. (2014)
Bismuth nanofilm	Flow injection analysis: amperometry	*E. coli*	Zhang et al. (2007)
Peptide nanotubes	Electrochemical: cyclic voltammetry	*E. coli*	Cho et al. (2008)
Gold	Surface plasmon resonance, electrochemical: cyclic voltammetry and differential pulse voltammetry	*E. coli*, *Staphylococcus aureus*, *Vibrio parahaemolyticus* and *Salmonella sps*	Zhao et al. (2007), Joung et al. (2008), and Afonso et al. (2013)
SWCNT	Field-effect transistor	*Salmonella infantis*	Villamizar et al. (2008)
Polypyrrole nanowires	Electrochemical: Linear sweep voltammetry	*Bacillus globigii*	Garcia-Aljaro et al. (2010)

6.2.1 Nanoparticle Based Detection of Food Pathogenic Bacteria

Pathogenic bacterial detection in food materials is mainly achieved by identifying the bacterial genetic material or whole bacterial cell. *Listeria monocytogenes* is a pathogenic bacterium found in milk. In this respect, paramagnetic nanoparticles were used for the isolation of *L. monocytogenes* deoxyribonucleic acid. Nanoparticles were functionalized with primer complementary to *Listeriolysin O* gene of *L. monocytogenes*. The deoxyribonucleic acid isolated from *L. monocytogenes* contaminated milk sample was quantified using polymerase chain reaction. Nanoparticles assisted deoxyribonucleic acid isolation and bacteria detection was less time consuming and more sensitive than other conventional methods (Amagliani et al. 2004). Carboxyl group functionalized magnetic iron oxide nanoparticles were also used for the isolation of *L. monocytogenes* from contaminated milk samples. The nanoparticles were covalently conjugated to amine group containing anti-*Listeria* antibodies. The immunocomplex was boiled to isolate deoxyribonucleic acid and quantified using real-time polymerase chain reaction (Yang et al. 2007).

The 16s ribosomal ribonucleic acid has been widely used as a selective marker for polymerase chain reaction based microbial detection. As the polymerase chain reaction based assay was costly, 16s ribosomal ribonucleic acid based microarray was alternatively developed for the detection of food contaminating pathogen, *L. monocytogenes* deoxyribonucleic acid. But this method lacks sensitivity (Call et al. 2003). Hence, nanoparticles based polymerase chain reaction free detection of 16s ribosomal ribonucleic acid was developed using gold nanoparticles as surface plasmon resonance detectors. This sensor could identify *Escherichia coli* and *Staphylococcus aureus* without the need of 16s ribosomal ribonucleic acid purification as required in case of polymerase chain reaction (Joung et al. 2008). Silver-enhanced fluorescence spectroscopy was recently coupled with bio-barcode assay for the sensitive detection of bacterial deoxyribonucleic acid. Magnetic nanoparticles were decorated with silver nanoparticles functionalized with single strand deoxyribonucleic acid. Separately a set of silver nanoparticles were also functionalized with double strand deoxyribonucleic acid containing fluorescently labeled barcodes. The presence of only test bacterial deoxyribonucleic acid allows the binding of two differently functionalized silver nanoparticles to form a hybrid structure. Thus, the bacterial deoxyribonucleic acid was specifically isolated by applying magnetic field and quantified using fluorescence spectroscopy. This method eliminates the extra step required for the liberation of barcodes (Zhou et al. 2014). Similarly, cadmium selenide-zinc sulphite quantum dots have been reported for the detection of *E. coli*. Quantam dots attached to magnetic beads were functionalized with single strand deoxyribonucleic acid probe. A capture deoxyribonucleic acid specific to *E. coli* deoxyribonucleic acid and a probe deoxyribonucleic acid were used to detect test deoxyribonucleic acid using fluorescence microscopy. Capture deoxyribonucleic acid binds the test deoxyribonucleic acid to magnetic bead, while probe deoxyribonucleic acid binds to the target deoxyribonucleic acid and fluorescent quantum dots. Further, quantum dots containing biotinylated linkers were attached to the quantum dots in order to enhance the sensitivity of detection (Liu et al. 2008).

Antibody-bacteria specificity was also explored for the detection of food pathogenic bacteria. Quantum dots have been used as fluorescent labels in immunoassay-assisted detection of *E. coli* and *Salmonella typhimurium*. Quantum dots with different emission wavelengths were conjugated to anti-*E. coli* and anti-*Salmonella* antibodies. Target bacteria were separated from samples by using specific antibody coated magnetic beads (Yang and Li 2006). Gold nanoparticles based immunosensors have also been reported for the detection of food borne pathogen, *Vibrio parahaemolyticus*. Agarose doped gold nanoparticles were used to immobilize horseradish peroxidase labeled anti-*V. parahaemolyticus* antibodies. Immobilization of antibodies in agarose doped gold nanoparticles were observed to enhance the amperometric response of the immunosensors. Bacteria interfered with horseradish peroxidase catalyzed oxidation of thionine. Thus, presence of *V. parahaemolyticus* induced alteration in current that was quantified using cyclic voltammetry (Zhao et al. 2007).

Bacillus globigii was used as a model to mimic bioterrorism-threatening agents like *Bacillus anthracis*. Polypyrrole nanowires functionalized with anti-*B. globigii* antibodies were used for the detection of *B. globigii* spores. Spores binds specifically to the antibody-modified nanowires mounted on the surface of electrode. Spore binding induces decrease in the flow of current to electrode (Garcia-Aljaro et al. 2010). In another such study, bismuth nanofilm modified glassy carbon electrode was reported for the detection of *E. coli*. β-D-glucuronidase enzyme catalyses the hydrolysis of 4-nitrophenyl β-D-glucuronide to 4-nitrophenol. *E. coli* produces 4-nitrophenyl β-D-glucuronide during its growth and development. So, the concentration of 4-nitrophenol was directly depending upon the concentration of *E. coli*. Since 4-nitrophenol is electroactive, its concentration was measured using cyclic voltammeter (Zhang et al. 2007). Anti-*E.coli* antibodies modified peptide nanotubes has also been used for the detection of *E. coli*. Nanotubes were deposited on the carbon electrode and binding of *E. coli* to electrode-induced change in current that was directly measured using cyclic voltammeter (Cho et al. 2008).

Semiconductor quantum dots have also been reported for the detection of foodborne pathogenic bacteria. Magnetic beads coated with anti-*E. coli* antibodies were used to capture *E. coli*. Further, addition of biotin-conjugated anti-*E. coli* antibodies formed sandwich immunocomplexes with *E. coli* bound to magnetic beads. Streptavidin labeled quantum dots bind specifically by this immunocomplex and change in fluorescence intensity was used to quantify *E. coli* (Su and Li 2004). The above documented studies have detected pathogenic bacteria in standard bacterial culture samples.

Nanoparticle based detectors have been employed for evaluating the microbial contamination in food samples. The presence of *E. coli* in milk was detected using amine-functionalized magnetic nanoparticles. The nanoparticles were first functionalized with avidin. Then the biotinylated anti-*E. coli* antibodies were immobilized on avidin, with *E. coli* recognition site facing outward. The magnetic nanoparticles bind specifically with *E. coli*. Hence, *E. coli* was then isolated from milk samples by applying a magnetic field. The captured *E. coli* cells were then quantified using adenosine triphosphate bioluminescence assay (Cheng et al. 2009). Likewise, gold nanoparticles have also been used to detect *Salmonella* from skimmed milk samples. *Salmonella* binds to the anti-*Salmonella* antibody containing magnetic beads. The conjugate was further incubated with gold nanoparticles modified with secondary antibodies. Thus, a sandwich immunocomplex containing *Salmonella* bound to magnetic bead and gold nanoparticles was formed. Immunocomplex was captured by a magnetic field on screen-printed carbon electrode surface and the electrochemical detection was carried out by differential pulse voltammetry (Afonso et al. 2013). Another strategy is to use anti-*E. coli* antibody conjugated magnetic nanoparticles. Antibody functionalized magnetic nanoparticles has been explored for developing impedance biosensors for the detection of *E. coli* in beef samples. Biotin-labeled polyclonal anti-*E. coli* antibodies were incubated with streptavidin-coated nanoparticles. Beef samples were incubated with functionalized nanoparticles to form *E. coli*-nanoparticle complexes. Complex formation increased the impedance of the system as was measured using impedance analyzer (Varshney et al. 2007; Varshney and Li 2007).

Likewise, consuming egg, chicken or meat contaminated with bacteria *Salmonella infantis* causes salmonellosis. Single-wall carbon nanotubes (SWCNT)-effect transistor biosensor has been developed for the detection of *S. infantis* in food samples. The sensing was based on the specific binding of anti-*Salmonella* antibodies functionalized SWCNT with *S. infantis*. *S. infantis* binding significantly decreased the electric current in a concentration dependent manner. So, the change in current was used to estimate the concentration of *S. infantis* (Villamizar et al. 2008). Anti-*E.coli* antibodies modified Tris-(2,2-bipyridyl) dichlororuthenium(II) hexahydrate doped silica nanoparticles has also been reported for the single cell detection of *E. coli* in beef samples. Several silica nanoparticles were attached to single *E. coli* through antigen-antibody interactions and was separated by centrifugation. The fluorescence of bacterial cell bound silica nanoparticles was recorded using spectrofluorometer and flow cytometer. This method was also useful for the detection of *S. typhimurium* and *B. cereus* spores in water samples (Zhao et al. 2004).

Iron oxide nanoparticles modified with antibodies have also been used for the simultaneous detection of *E. coli* and *S. typhimurium* in milk and spinach samples. The process of detection involved antibody specific binding of microbes on nanoparticles surface that resulted in the alteration of nanoparticle characteristic peaks in fourier transform infrared spectra (Ravindranath et al. 2009). Nanoparticles have, thus taken up the process of biological entity sensing to a single cell level. Nanoparticle based sensors even have the ability to detect multiple targets at a time with enhanced sensitivity in complex biological and food materials (Alivisatos 2004).

6.2.2 Nanoparticle Based Detection of Food Contaminating Toxins

Aflatoxins are a group of toxic and carcinogenic compounds found in food contaminated with *Aspergillus flavus* and *Aspergillus parasiticus*. Gold nanoparticles functionalized with anti-aflatoxin antibodies has been used as sensor for the detection of aflatoxin B1 (Table 6.2). The gold nanoparticles were mixed with 4-mercaptobenzoic acid to form monolayer on gold electrode. The functional sites of antibody bound to gold nanoparticles were blocked with bovine serum albumin. Bovine serum albumin binding to gold nanoparticles decreased the current flow. However, presence of aflatoxin in sample displaced bovine serum albumin and enhanced the current flow in concentration dependent manner (Sharma et al. 2010).

Table 6.2 Nanomaterial based detection of food contaminating toxins

Type of nanoparticle	Method/technique	Analyte	References
Gold	Electrochemical: cyclic voltammetry, immunochromatographic, dynamic light scattering and enzyme-linked immunosorbent assay	Botulinum neurotoxin type B, aflatoxin B1 and brevetoxins	Chiao et al. (2004), Xiulan et al. (2005), Zhou et al. (2009), Sharma et al. (2010), Wang et al. (2011), and Zhang et al. (2013a)
Iron oxide	Immunoassay and enzyme-linked immunosorbent assay	Aflatoxins B1, aflatoxin M1 and mycotoxin: zearalenone and HT-2	Radoi et al. (2008) and Mak et al. (2010)
Cerium dioxide	Electrochemical: cyclic voltammetry	Ochratoxin-A	Kaushik et al. (2009)
SWCNT	Immunoassay	Microcystin-LR	Wang et al. (2009)
Quartz nanopipettes	Ion nano-gating	Mycotoxin HT-2	Actis et al. (2010)
Zinc oxide	Electrochemical: impedance spectroscopy and cyclic voltammetry	Ochratoxin-A	Ansari et al. (2010)
Gold-graphene oxide-ionic liquid	Electrochemical: cyclic Voltammetry	Ochratoxin-A	Norouzi et al. (2012)
MWCNT	Electrochemiluminescence	Palytoxin	Zamolo et al. (2012)

Likewise, superparamagnetic beads containing anti-aflatoxin M1 antibodies and gold nanoprobes have also been used for the detection of aflatoxin M1 in milk samples. Gold nanoprobes containing anti-aflatoxin M1 and bovine serum albumin bind to antibodies on magnetic beads in absence of aflatoxin M1 (Fig. 6.3). In aflatoxin M1 contaminated samples, the aflatoxin M1 displaced nanoprobes by competitive binding to antibodies. The concentration of free nanoprobes was measured using dynamic light scattering reading that was proportional to quantity of aflatoxin M1 in samples (Zhang et al. 2013a).

Immuno-chromatographic strip assay has also been documented for the detection of pathogenic bacteria. Nanoparticle modified strips have better sensitivity than conventional immuno-chromatographic strips. Gold nanoparticles based immuno-chromatographic strip method has been employed for the detection of aflatoxin M1 in milk. The strip contains embedded ovalbumin-aflatoxin M1 complex bound to colored gold nanoparticles containing anti-aflatoxin M1 antibodies. Thus a red color band appears on the strip. The aflatoxin M1 competes with ovalbumin-aflatoxin M1 complex for binding with colored gold nanoparticles. The strip was

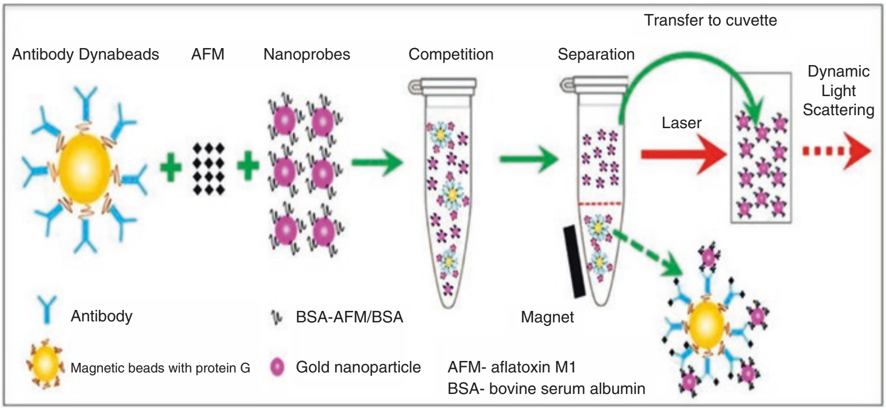

Fig. 6.3 Dynamic light scattering detection of aflatoxin M1 using gold nanoparticle based probes (Figure adapted with permission from (Zhang et al. 2013a). Copyright (2013) American Chemical Society)

washed to remove free aflatoxin-gold nanoparticles complex. The aflatoxin contaminated milk sample appears as colorless zone on the strip (Wang et al. 2011). Superparamagnetic nanoparticles has been used for improving the efficiency of direct competitive enzyme-linked immunosorbent assay for aflatoxin M1 detection in milk. The use of nanoparticles reduced the time of coating, blocking and competition steps of enzyme-linked immunosorbent assay from 12–24 h to mere 20 min (Radoi et al. 2008).

Contaminated seafood generally, contains marine toxin, palytoxin. Carbon nanotubes based electro-chemiluminescent sensors have been designed for the ultrasensitive detection of palytoxin in mussel meat. Palytoxin monoclonal antibody functionalized nanotubes were deposited on the optically transparent electrode. As the electrode was exposed to meat sample, monoclonal antibodies bind to palytoxin. The electrode was further exposed to polyclonal antibody labeled with the electrochemiluminescent probe. So, the chemiluminescence intensity was used to estimate the concentration of palytoxin in mussel meat (Zamolo et al. 2012). Zinc oxide nanoparticles has been reported for the detection of ochratoxin-A, food-contaminating mycotoxin. Ochratoxin-A has teratogenic, carcinogenic, nephrotoxic and immunotoxic activity. Zinc oxide nanoparticles film deposited onto indium-tin-oxide glass plates were used as impedimetric sensors for the detection of ochratoxin-A (Ansari et al. 2010). Gold nanoparticles-graphene nanosheets oxide-ionic liquid nanocomposites have also been documented for the detection of ochratoxin-A (Norouzi et al. 2012). Antibody functionalized cerium oxide nanoparticles film has been used as biosensor for detecting ochratoxin-A. Positively charged cerium oxide nanoparticles bind to carboxyl group of antibodies due to electrostatic interactions. The free amino terminal sites of antibodies bind to the carboxylic group of ochratoxin-A. The formation of an antigen-antibody complex thus, increased the current flow to electrode (Kaushik et al. 2009).

Quartz nanopipettes have been used as electrochemical biosensors for the detection of mycotoxin HT-2. Quartz capillaries were pulled with laser puller to produce 50 nanometer quartz nanopipettes. The nanopipettes were further functionalized with anti-HT-2 antibodies. Silver/silver chloride wire was inserted into nanopipettes to comprise a signal transduction by ion nano-gating electrode to measure the current. HT-2 toxin binds to the antibodies present on the inner nanopipette surface and blocks the current flow inside the nanopipette (Actis et al. 2010). Detection of multiple mycotoxins, aflatoxins B1, zearalenone and HT-2 has been reported by using magnetic nanotags based sandwich immunoassays. Anti-mycotoxin antibodies were immobilized on the nanotags. The nanotags were incubated with the mixture of mycotoxin followed by exposure of biotin containing detection antibodies. Detection antibody containing streptavidin coated nanotags bind specifically to mycotoxin and was quantified by the magnitude of magnetic signal (Mak et al. 2010).

Similarly, an immunochromatographic strip was developed to detect botulinum neurotoxin type B. As the strip is placed in solvent, gold nanoparticle-rabbit anti-botulinum neurotoxin type B antibody conjugate travel by capillary action and bind to goat anti-rabbit antibodies in the control detection region of strip. As the sample containing neurotoxin is carried to detection reagent zone containing gold nanoparticle-rabbit anti-botulinum neurotoxin type B antibody conjugate, neurotoxin binds neurotoxin antibodies conjugated gold nanoparticle probes and form a complex. This complex travel by capillary action of solvent and is trapped by rabbit anti-botulinum neurotoxin type B antibodies and appear as pink band in test region of strip (Chiao et al. 2004). Strip based immunochromatographic assay has also been reported for brevetoxin detection in fishery products. In detection zone, control region contained goat anti-mouse immunoglobulin G, while test region contained brevetoxin-bovine serum albumin. Gold nanoparticles-monoclonal antibodies bind to test as well as control region in absence of toxin. However in presence of toxin, the gold nanoparticles probe binds with toxin. As a result quantity of gold nanoparticle probe binding to bovine serum albumin-brevetoxin in test region is reduced. Higher the toxin concentration, lower is the color intensity of the test line (Zhou et al. 2009). Aflatoxin B1 polyclonal antibodies were conjugated to gold nanoparticles to form aflatoxin probe. This probe was applied to strip such that, in case of presence of afaltoxin B1 in the test sample, the zone appeared colorless (Fig. 6.4). While same zone appeared colored in absence of aflatoxin (Xiulan et al. 2005).

In a simple experiment, microcystin-LR antibodies functionalized SWCNTs were adsorbed on the filter paper to detect microcystin-LR. Microcystin-LR is a toxin produced by the cyanobacteria. It is generally found in contaminated water. Toxin detection is based on the measurement of reduction in the current passage through SWCNT containing filter paper electrode. Microcystin-LR binding to SWCNT hinders the current flow to electrode (Wang et al. 2009).

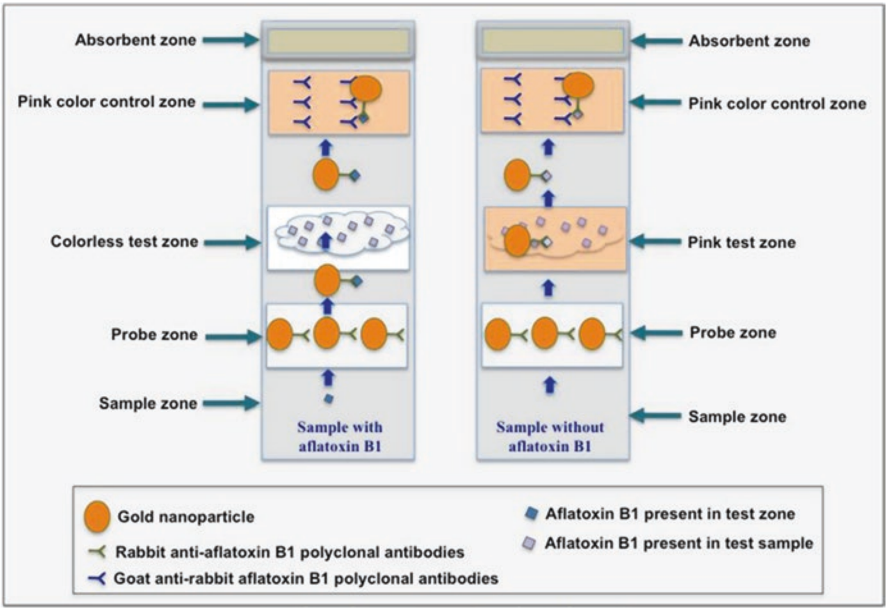

Fig. 6.4 Figure showing the basic setup and functioning of gold nanoparticle based aflatoxin B1 immunoassay. The flow of solvent is from *bottom* to *top*. Adsorbent is at *top* and the solvent flow is due to capillary action of membrane

6.2.3 Nanoparticle Based Detection of Food Contaminating Pesticides and Chemicals

Nanoparticles have been used for the detection of pesticides, fertilizer sand other toxic chemicals (Table 6.3). Pesticides have extensively been used in many agricultural and industrial processes. Among the various pesticides, organophosphates are the most commonly used pesticides. Organophosphates are highly toxic, so their contamination in food is a serious concern (Vamvakaki and Chaniotakis 2007). Gold nanoparticles have been used as colorimetric and fluorometric sensors for the detection of pesticides in food products. The gold nanoparticles were functionalized with rhodamine-B such that the solution appeared red and the fluorescence of rhodamine was quenched. On adding acetylcholinesterase enzyme and its substrate, the color of gold nanoparticles solution changed to blue and the fluorescence of rhodamine was simultaneously unquenched. Acetylcholinesterase produces thiocholine that has induced aggregation of gold nanoparticles and hence color of nanoparticles change from red to blue. Organophosphorus and carbamate pesticides inhibited the activity of acetylcholinesterase. As a result, the gold nanoparticles solution changed from blue to red and the fluorescence of rhodamine was quenched (Liu et al. 2012). Similarly, acetylcholinesterase was encapsulated with a pH sensitive fluorescence indicator inside liposomes. Acetylcholinesterase converts acetylcholine in the test

Table 6.3 Nanoparticle based detection of food contaminating pesticides and chemicals

Type of nanoparticle	Method/technique	Analyte	References
Zinc sulfide-cadmium selenide and thioglycolic acid-cadmium selenide	Photoluminescence spectroscopy	Paraoxon	Constantine et al. (2003) and Ji et al. (2005)
Liposome	Fluorescence spectroscopy	Organophosphorus pesticides	Vamvakaki and Chaniotakis (2007)
MWCNT	Electrochemical: cyclic voltammetry and solid-phase extraction-high-performance liquid chromatography	Sudan I	Ming et al. (2008), Gan et al. (2008), Wu (2010), Wu et al. (2013a), and Yang et al. (2010)
Zirconium dioxide-gold	Electrochemical: square wave voltammetry	Parathion	Wang and Li (2008)
SWCNT	Field-effect transistor	Bisphenol A	Sanchez-Acevedo et al. (2009)
Graphene	Electrochemical	Sudan I	Ma et al. (2013)
Iron oxide	Electrochemical	Sudan I	Yin et al. (2011)
Gold	Fluorescence spectroscopy, colorimetric and ultraviolet-visible spectroscopy	Melamine, organophosphorus and carbamate pesticides	Huang et al. (2011), Kuang et al. (2011), Su et al. (2011), Liu et al. (2012), and Vasimalai and John (2013)
Silver	Colorimetric and ultraviolet-visible spectroscopy	Melamine	Han and Li (2010), Ping et al. (2012)
Cobalt nitroprusside	Electrochemical: cyclic voltammetry	Sulfite	Devaramani and Malingappa (2012)
MWCNT- Silica, MWCNT-zinc oxide, MWCNT-platinium and MWCNT-ionic liquids	Electrochemical: cyclic voltammetry	Sudan I, bisphenol A, cadmium ions, sunset yellow and tartrazine	Bagheri et al. (2013), Elyasi et al. (2013), Majidi et al. (2013),and Najafi et al. (2014)
Poly(ethylene glycol dimethacrylate-N-methacryloyl-L-histidine methylester)	Ultraviolet-visible spectroscopy: surface plasmon resonance	Chloramphenicol	Kara et al. (2013)
Cadmium telluride quantum dots	Fluorescence	Melamine	Xu and Lu (2015)

solution to choline and acetic acid. Acetic acid reduces pH and activates the fluorescent indicator pyranine. While in presence of organophosphorus pesticides dichlorvos and paraoxon, the enzymatic activity is inhibited and hence, the fluorescence was quenched (Vamvakaki and Chaniotakis 2007).

Photoluminescence properties of quantum dots have also been explored for sensing pesticides. The pesticide paraoxon has been reported to quench the photoluminescence of organophosphorus hydrolase conjugated cadmium selenide zinc sulfide core-shell quantum dots in concentration dependent manner. The reduction in photoluminescence was due to conformational change in the structure of enzyme (Ji et al. 2005). Polyelectrolyte film containing organophosphorus hydrolase and thioglycolic acid-capped cadmium selenide quantum dots has also been reported for the detection of paraoxon. The film appeared green upon epifluorescence imaging in the absence of paraoxon. However in the presence of paraoxon, quantum dots lost their photoluminescence and hence film becomes non-fluorescent (Constantine et al. 2003). Selective binding of phosphate group containing pesticide parathion to zirconium dioxide/gold nanocomposite film electrode has been employed for developing voltametric biosensors (Wang and Li 2008). MWCNT-silica nanocomposite based potentiometer sensors have been documented for the detection of toxic cadmium ions. Nanocomposite material was used to modify carbon paste electrode. Cadmium ion binds to nanocomposite material and induces decrease in the electrode potential of carbon paste (Bagheri et al. 2013).

Like pesticides, excessive use of fertilizers is also a big concern. Melamine is a fertilizer. It shows analytic properties of protein due to its high nitrogen content. So, it is used to adulterate protein rich products such as egg, biscuits, candy and coffee drinks. Melamine binds to gold nanoparticles due to its multiple amine groups. On addition of micromolar concentration of melamine, the gold nanoparticles were aggregated and the color of gold nanoparticles changed from wine red to purple. Reduction in ultraviolet-visible absorption peak respective to gold nanoparticles was also observed. However, picomolar concentration of melamine did not induce aggregation. Rather interestingly, melamine has induced selective increment in the fluorescence intensity of gold nanoparticles at picomolar concentration. Using this strategy, picomolar concentration of melamine was detected in cow milk and infant formulas (Vasimalai and John 2013). Ether functionalized gold nanoparticles were also employed for the detection of melamine. Melamine binding to gold nanoparticles has induced shift in the ultraviolet-visible absorption spectra of ether capped gold nanoparticles (Kuang et al. 2011). Further, gold nanoparticles have also been used to develop selective colorimetric detectors for detections of melamine in milk. In the presence of sodium chloride containing medium, polythymine binds to gold nanoparticles surface and prevent their aggregation. While in presence of melamine, polythymine binds to melamine by hydrogen bonding and gold nanoparticles undergo aggregation in a melamine concentration dependent manner. The color of gold nanoparticles changes from red to blue upon aggregation, with simultaneous reduction in the ultraviolet-visible absorption peak of gold nanoparticles (Huang et al. 2011). Similarly, colorimetric sensing of melamine by 3-mercapto-1-propanesulfonate modified gold nanoparticles has been reported. Melamine forms hydrogen bond with 3-mercapto-1-propanesulfonate and induces aggregation of gold nanoparticles in presence of sodium chloride. So, the gold nanoparticles color changes from red to blue in presence of melamine (Su et al. 2011).

Likewise, p-nitroaniline capped silver nanoparticles were aggregated on addition of melamine and the color of solution changed from yellow to blue. Further, shift in the ultraviolet-visible absorption peak maxima was also noticed. Aggregation was due to electron donor-acceptor interaction between melamine and nanoparticles (Han and Li 2010). Melamine induced aggregation of silver nanoparticles has also been used as basis for developing melamine detection colorimetric sensors. The color of silver nanoparticles changed from yellow to red in presence of melamine. This method could detect micromolar concentration of melamine in raw milk (Ping et al. 2012). Spectrofluorometery is also used for the detection of melamine. Melamine induced concentration dependent quenching of fluorescence intensity of cadmium telluride quantum dots (Xu and Lu 2015).

Food dyes and preservatives are also toxic when used above permissible limit. MWCNT-ionic liquid nanocomposites modified carbon-ceramic electrodes have been used for the detection of food dyes. Nanocomposites induced electro-catalytic oxidation of dyes, sunset yellow and tartrazine. Thus, the dyes generated separate oxidation peaks. Hence, simultaneous determination of these two dyes was possible (Majidi et al. 2013). Sulfite is commonly used as preservative in food and beverages, but it is toxic and allergic above certain concentration. So, highly sensitive methods are required to detect sulfite in trace amounts. Cobalt nitroprusside nanoparticles has been used for the detection of sulfite in sugar, dry fruits and wine. Nanoparticles induced electrocatalytic oxidation of sulfite thus leading to increase in the magnitude of anodic peak current. The change in peak current was measured using cyclic voltammeter (Devaramani and Malingappa 2012).

Chloramphenicol is a broad-spectrum antibiotic. It has ill effect on human health. Hence, the use of chloramphenicol in bees and animals is restricted due to the chances of derived food product contamination. But it is still used to cure infections in bees due to low cost. Hence, bee honey gets contaminated with antibiotics. Poly(ethylene glycol dimethacrylate-N-methacryloyl-L-histidine methylester) nanoparticles has been used for the detection of chloramphenicol in honey samples. Nanoparticles were imprinted on the surface of surface plasmon resonance active gold nanosensor chip such that chloramphenicol was adsorbed on the nanoparticle surface. Chloramphenicol adsorption induces concentration dependent change in surface plasmon resonance signal of nanosensor (Kara et al. 2013).

Sudan I is a carcinogenic red dye. Due to its red color, it has been used as adulterant in chili powder. Multi-wall carbon nanotubes (MWCNT) has been used for the detection of Sudan I adulteration in chili powder. MWCNT modified electrode catalyzes the reduction of Sudan I to generate peak in cyclic voltammeter. Hence, the peak intensity depends upon the concentration of Sudan I (Ming et al. 2008; Yang et al. 2010). Likewise, MWCNT-chitosan nanocomposites were used for the electrochemical detection of Sudan I in chili powder. MWCNT paste is prepared for electrode modification. Organic solvents that are used for preparing MWCNT paste are toxic. Chitosan increased the water solubility of MWCNT in aqueous medium.

Thus, chitosan prevented the use of toxic organic solvents by replacing them (Wu et al. 2013a). SWCNT-iron porphyrin modified electrode also catalyses the electrochemical reduction of Sudan I. Iron porphyrin was mainly responsible for the electrochemical reduction of Sudan I (Wu 2010). Graphene modified electrode has also been used for the detection of Sudan I in chilli sauce and ketchup. The sensitivity of nanosensor was increased in the presence of surfactant, sodium dodecyl sulphonate. Sodium dodecyl sulphonate facilitated the better adsorption of Sudan I on graphene surface. This enhances the electrochemical reduction of Sudan I (Ma et al. 2013). Sudan I oxidation on the surface of MWCNT and platinum-carbon nanotube nanocomposite modified electrodes has also been explored for designing sensor (Gan et al. 2008; Elyasi et al. 2013). Likewise, iron oxide nanoparticle modified electrode has also been employed for Sudan I detection in chilli powder, chilli sauce, strawberry sauce, tomato sauce, ketchup and egg yolk (Yin et al. 2011).

SWCNT field-effect transistor based biosensor has been designed for the detection of bisphenol A. Bisphenol A is a toxic contaminant released from plastic container. SWCNT field-effect transistor was modified using a layer of estrogen receptor alpha. Bisphenol A binding to receptor has induced a concentration dependent decrease in the electrode current (Sanchez-Acevedo et al. 2009). MWCNT-zinc oxide nanocomposite has been documented for the detection of bisphenol A and Sudan I. Nanocomposite induced electrocatalytic oxidation of bisphenol A and Sudan I. The oxidation peaks of bisphenol A and Sudan I were observed at different positions. So, the simultaneous detection of bisphenol A and Sudan I was possible (Najafi et al. 2014).

6.3 Nanomaterial Based Sensors for Food Freshness Detection

The food ingredients generally get spoiled on storage longer than shelf life and exposure of air and moisture. Laboratory based food spoilage testing is not possible for individual packages. Alternatively, on-spot indicators are cost-effective, easy and sensitive. Use of nanoparticles has proved efficient for developing on-spot detectors to check food spoilage arising due to moisture, oxygen and microbes. Also, nanoparticles based on-spot indicators can be easily labeled on individual packages (Realini and Marcos 2014; Jiang et al. 2015).

6.3.1 Food Quality Assessment Due to Improper Storage

Besides adulteration and contamination by bacteria or toxin, some food products are perishable and prone to degradation. Some food items are stable at particular temperature and limited storage time. But these food materials perish on change in

Table 6.4 Nanomaterial based time-temperature indicators for food freshness: nanomaterial based food freshness indicators/detectors

Type of nanoparticle	Method/technique	Indicator type	References
Zinc oxide	Electrical	Time: trimethylamine	Tang et al. (2006)
Gold	Colorimetric: ultraviolet-visible spectroscopy and electrochemical: cyclic voltammetry	Thermal history and time: xanthine and hypoxanthine	Cubukcu et al. (2007), and Wang et al. (2015a)
Methylene blue-titanium dioxide	Colorimetry	Oxygen	Gutierrez-Tauste et al. (2007)
Tin dioxide-zinc oxide	Electrical: gas sensing	Time: trimethylamine	Zhang and Zhang (2008)
Poly-(styreneblock-vinylpyrrolidone)	Luminescence	Oxygen	Borisov and Klimant (2009)
Silver	Colorimetric: ultraviolet-visible	Time-temperature	Zeng et al. (2010)
Iron oxide-titanium dioxide	Electrochemical: voltammetry and intelligent test system	Trimethylamine	Lou et al. (2013)
Silver shell gold nanorods	Colorimetric: ultraviolet-visible	Time-temperature	Zhang et al. (2013b)
Polydiacetylene-silica	Colorimetric: ultraviolet-visible	Time-temperature	Nopwinyuwong et al. (2014)

storage time and temperature. Time-temperature indicators are used to monitor freshness of such food items. Traditional time-temperature indicators are costly and lack flexibility in programming. So nanoparticles based time-temperature indicators has been developed to overcome these limitations. Time and temperature dependent intrinsic structural instability and color changes in triangular silver nanoplates have been explored for the generation of time-temperature sensors (Table 6.4). The silver nanoplates changes shape in time-temperature dependent manner from triangular to spherical shape. The nanoplates also undergo blueshift in ultraviolet-visible absorbance with increase in temperature and passage of time (Zeng et al. 2010). Similarly, the color of polydiacetylene/silica nanocomposites changes from purplish-blue to red in time-temperature dependent manner, which forms the basis of time-temperature sensors (Nopwinyuwong et al. 2014). Silver shell gold nanorods have been used to develop cost-effective indicators for perishable items. The red colored gold nanorods undergo conversion to green colored silver shell gold nanorods in time-temperature dependent manner. Milk quality is degraded if stored at high temperature for long time. So, these nanorods were used to detect the degradation of milk quality (Zhang et al. 2013b). Gelatin stabilized gold nanoparticles undergo temperature and time dependent change in color, size and shape. This property of gold nanoparticles has been employed to develop thermal history indicators for perishable items (Wang et al. 2015a).

Freshness of packed food items is reduced on exposure to oxygen. Oxygen promotes the oxidation of antioxidants and hence, induces the growth of bacteria. So, it is desirable to check the oxygen exposure in packed foodstuffs. Light-activated colorimetric oxygen indicators have been produced for this purpose using methylene blue/titanium dioxide hybrid nanocomposite material. Exposure of ultraviolet light generated electrons that reduced the blue colored methylene blue dye to transparent leuco form. The leuco form remained stable in absence of oxygen. However, the leuco-methylene blue form is reoxidized to blue colored compound in the presence of oxygen. Along with colorimetric change, the change in current on oxygen exposure was also analyzed using cyclic voltammeter (Gutierrez-Tauste et al. 2007). Oxygen sensor was also developed using luminescent metal-ligand complex functionalized poly-(styreneblock-vinylpyrrolidone) nanobeads. The luminescence of complex was quenched in presence of oxygen. The oxygen concentration was, thus estimated by measuring the lifetime and intensity of luminescence (Borisov and Klimant 2009).

Trimethylamine is generally produced as a result of metabolism of animal proteins with passage of time. So, presence of trimethylamine is also an indicator of loss of freshness. Trimethylamine has been reported to show loss of freshness in fishes and seashells. Tin dioxide-zinc oxide nanocomposite sensors were effectively employed for the detection of trimethylamine in fish samples. Trimethylamine induces increase in electrode current in concentration dependent manner. Tin dioxide nanoparticles doping with zinc oxide microrods increase the transfer of charge to electrode. Thus, zinc oxide doping improves the trimethylamine sensing efficiency of tin dioxide nanoparticles (Zhang and Zhang 2008). Like zinc oxide microrods, polyvinylpyrrlidone capped zinc oxide nanoparticles have also been used for trimethylamine sensing. Trimethylamine induced increase in sensor current. Polyvinyl pyrrolidone modification of zinc oxide nanoparticles improved their crystallization and provide stability to zinc oxide nanoparticles (Tang et al. 2006). Branched iron oxide-titanium dioxide hetero-nanostructure has also been used for trimethylamine sensing. Nanostructures adsorb trimethylamine on their surface and catalyses its oxidation to generate electron. Electrons were then transferred to electrode and measured (Lou et al. 2013).

Electrodes modified with gold nanoparticles and xanthine oxidase enzyme has also been used for estimating the freshness of animal meat. Xanthine and hypoxanthine found in meat undergoes degradation with time to release hydrogen peroxide. Hydrogen peroxide is further degraded to generate electrons. Presence of gold nanoparticles increased the activity of xanthine oxidase enzyme as well as electron transfer between the enzyme and electrode. So, electrode containing gold nanoparticles possessed better sensitivity as compared to standard electrodes (Cubukcu et al. 2007).

6.3.2 Sensing the Quality of Unstable Key Food Ingredients During Food Processing and Storage

Vitamins and other antioxidant components present in food products are degraded very easily. These components provide resistance against diseases along with nutrition. Deficiency of water-soluble vitamin folic acid can cause anemia, carcinogenesis and heart attack. United States and United Kingdom has introduced mandatory fortification of cereal grain and flour with folic acid to counter its deficiency. Glassy carbon electrode modified using SWCNT-ionic liquids nanocomposites have been reported for the detection of folic acid in wheat flour, fruit juices and milk samples. The nanocomposite induced oxidation of folic acid (Xiao et al. 2008). MWCNT modified gold electrode was also used for the electrocatalytic oxidation of folic acid. The current generated due to electrochemical oxidation of folic acid was measured using cyclic voltammeter (Wei et al. 2006). Similarly, 2,2′-[1,2-ethanediylbis (nitriloethylidyne)]-bishydroquinone double-wall carbon nanotube and ferrocenedicarboxylic acid functionalized MWCNT paste electrodes has also been used for the electrochemical sensing of folic acid (Beitollahi et al. 2008; Ensafi and Karimi-Maleh 2010).

Nickel oxide nanoparticles have been used for the detection of vitamin, ascorbic acid. Nanoparticles catalyzed the electro-oxidation of ascorbic acid. This electrochemical process was measure using cyclic voltammeter (Table 6.5). This nanosensor was used for ascorbic acid detection in chilli sauce, tomato sauce, fruit juice and vegetable juice (Karimi-Maleh et al. 2014). Likewise, N-(3,4-Dihydroxyphenethyl)-3,5-dinitrobenzamide modified-MWCNT paste electrode induced electrocalytic oxidation of ascorbic acid and essential amino acid, tryptophan. The ascorbic acid and tryptophan concentration was directly correlated with the current produced. The current was measured using cyclic voltammeter (Ensafi et al. 2012).

The antioxidant value of red wine is due to its phenolic content. Tyrosinase enzyme immobilized gold nanoparticles modified glassy carbon electrode undergoes change in electrochemical potential on exposure to phenolic compound. Enzyme induces oxidation of phenol moieties into corresponding o-quinones. This electrochemical process was used to detect the quality of phenol in red and white wines. Gold nanoparticles ensured good catalytic activity and hence, good analytical performance of the biosensor (Liu et al. 2003; Sanz et al. 2005).

Hydrogen peroxide is used as an antioxidant in food industry, but it may decompose in food products if not stored properly. Further, higher concentration of hydrogen peroxide can induce toxic effects in humans. Poly-(vinyl alcohol) capped silver nanoparticles react with hydrogen peroxide and as a result, the strength of localized surface plasmon resonance of silver nanoparticles changes. The yellow color of silver also changed to transparent on reaction with hydrogen peroxide. The silver nanoparticles were easily regenerated by heat treatment (Filippo et al. 2009). Silver nanoparticles modified glassy carbon electrode induced decomposition of hydrogen peroxide to water and oxygen. Oxygen was further reduced on the surface of silver nanoparticles and the electro-reduction signal was measured using voltammeter

Table 6.5 Nanomaterial based detection of unstable key food ingredients

Type of nanoparticle	Method/technique	Analyte	References
Gold	Electrochemical: cyclic voltammetry and amperometry	Glucose, catechol, caffeic acid, chlorogenic acid, gallic acid and protocatechualdehyde	Liu et al. (2003), Sanz et al. (2005), and Li et al. (2007)
MWCNT	Electrochemical: cyclic voltammetry and voltammetry	Hydrogen peroxide, glucose, ascorbic acid, acetaminophen, tryptophan and folic acid	Wang et al. (2003), Ye et al. (2004), Wei et al. (2006), Xiao et al. (2008), Ensafi and Karimi-Maleh (2010), Ensafi et al. (2012), and Scandurra et al. (2013)
Diphenylalanine peptide nanotubes	Electrochemical: cyclic voltammetry	Glucose	Yemini et al. (2005)
Silver	Ultraviolet-visible spectroscopy: localized surface plasmon resonance and electrochemical: cyclic voltammetry	Hydrogen peroxide	Welch et al. (2005) and Filippo et al. (2009)
2,2′-[1,2-ethanediylbis(nitriloethylidyne)]-bishydroquinone double-wall carbon nanotube	Electrochemical: cyclic voltammetry	Folic acid	Beitollahi et al. (2008)
Copper-chitosan-SWCNT	Electrochemical: amperometry	Glucose and hydrogen peroxide	Wang et al. (2008)
Zirconium dioxide	Electrochemical: cyclic voltammetry	Hydrogen peroxide	Liang and Mu (2008)
SWCNT	Electrochemical: cyclic voltammetry	Folic acid	Xiao et al. (2008)
Iron-nickel-platinum	Electrochemical: cyclic voltammetry	Hydrogen peroxide	Liu et al. (2010)
Prussian blue-gold	Electrochemical: cyclic voltammetry	Hydrogen peroxide	Chen et al. (2011)
Cuprous oxide	Electrochemical: cyclic voltammetry	Hydrogen peroxide	Yan et al. (2013)
Carbon-tin dioxide-platinum	Electrochemical: cyclic voltammetry	Hydrogen peroxide	Lu et al. (2013)

(continued)

Table 6.5 (continued)

Type of nanoparticle	Method/technique	Analyte	References
Silver-tin dioxide	Adsorption	Ethanol	Wu et al. (2013b)
Platinum-cobalt	Voltammetry	Vitamin B_9 and folic acid	Jamali et al. (2014)
Nickel oxide	Electrochemical	Ascorbic acid	Karimi-Maleh et al. (2014)

(Welch et al. 2005). Zirconium dioxide nanoparticles were electrodeposited on the gold electrode and coated with double stranded deoxyribonucleic acid-doped hemoglobin mixture to develop hydrogen peroxide sensor. Zirconium dioxide nanoparticles act as inert immobilization support and helps in maintaining the catalytic activity of hemoglobin. Hydrogen peroxide undergoes reduction in the presence of hemoglobin to induce amperometric response in concentration dependent manner (Liang and Mu 2008). Some reports, as shown in Table 6.5 have documented the use of MWCNT, cuprous oxide nanowires, carbon-coated tin dioxide supported platinum nanoparticles, prussian blue-gold nanocomposite and iron-nickel-platinum nanoparticles for sensing hydrogen peroxide (Liu et al. 2010; Chen et al. 2011; Scandurra et al. 2013; Yan et al. 2013; Lu et al. 2013).

The level of glucose, fructose, sucrose, D-sorbitol, L-malic acid, citric acid, succinic acid, L-glutamic acid, hydrogen peroxide and alcohol during food processing and stored product is used as indicators of food quality (Verstrepen et al. 2004; Terry et al. 2005; Vermeir et al. 2007). MWCNT modified glassy carbon electrode catalyses the electrocatalytic oxidation of glucose to generate electrons. The current generated was measured using cyclic voltammeter. The electrocatalytic activity of electrode was due to the thin layer of cobalt present at the surface of MWCNTs (Ye et al. 2004). While diphenylalanine peptide nanotubes were functionalized with glucose oxidase to detect glucose. Nanotubes were coated on the surface of gold electrode. Glucose oxidase produced hydrogen peroxide in the presence of glucose. Hydrogen peroxide was further oxidized to produce electrons that were detected using voltammeter (Yemini et al. 2005). Amperometric MWCNT/gold film based biosensor has been designed for glucose detection. Glucose oxidase enzyme enters MWCNT and gets immobilized. Interaction of enzyme with carboxylic acid groups of nanotubes enhances the stability and sensitivity of nanosensor. Glucose oxidase catalyses the oxidation of glucose to gluconic acid. The electrons generated as a result of glucose oxidation were measured to sense the concentration of glucose (Wang et al. 2003). Similarly, glucose oxidase functionalized gold nanoparticles and copper-chitosan-SWCNT nanocomposites were immobilized on glassy carbon electrode to produce glucose biosensors (Li et al. 2007; Wang et al. 2008).

6.4 Nanobarcodes for Product Authenticity

Barcodes are globally used as product authentication labels. Two-dimensional barcodes are commonly used these days. But these barcodes can be easily located and hence, are more prone to damage, alteration and falsification. However at the same time, nanoparticle based invisible barcodes can be labeled without being noticed. So, the nanobarcodes are hard to manipulate (Wang et al. 2015b). Unique nanoparticle based encoding system and nanodisk codes have been reported recently (Table 6.6). Nanodisk code is a sequence of surface-enhanced raman scattering producing disk pairs that can be scanned with Raman microscope. Authors have tailored linear arrays of gold nanodisk pairs using on-wire lithography. The nanodisk pairs were functionalized with Raman chromophores, methylene blue and para-mercaptoaniline. The nanodisk codes were generated by varying the number and location of the pairs. Five gold nanodisk pairs were used in the study and thirteen binary codes were generated. Physical presence and absence of nanodisk pair was stored as 1 and 0 codes, respectively. Further, spectroscopic fingerprints of the Raman chromophores adsorbed on gold nanodisk were used as additional chemical labels (Qin et al. 2007).

Similarly, silver nanodisk and silver-gold heterodimer nanodisk codes have also been reported. Silver nanodisks showed better surface-enhanced Raman scattering than gold nanodisks. The efficiency of silver-gold heterodimer was better than silver-silver and gold-gold homodimers due to the transfer of plasmon energy from silver disk to gold disk (Qin et al. 2006; Banholzer et al. 2010; Liusman et al. 2012).

Table 6.6 Nanobarcodes for product authenticity

Type of nanoparticle/nanobarcode	Method/technique	Analyte	References
Deoxy ribonucleic acid	Fluorescence microscopy, dot blotting and flow cytometry	*E. coli*, anthrax, tularemia, ebola and severe acute respiratory syndrome virus	Li et al. (2005)
Gold-nickel	Scanning confocal Raman spectroscopy	Deoxyribonucleic acid	Qin et al. (2006, 2007)
Silver-gold	Scanning confocal Raman spectroscopy	Barcode and deoxyribonucleic acid	Banholzer et al. (2010), Liusman et al. (2012)
Poly(p-phenylene vinylene)	Photoluminescence spectroscopy	Barcode	Li et al. (2010)
Chromium-nickel	Charge-coupled device detector	Barcode	Banu et al. (2006)
Chromium	Charge-coupled device detector	Barcode	Birtwell et al. (2008)
Deoxy ribonucleic acid	Total internal reflection fluorescence microscopy	Barcode	Lin et al. (2012)

This approach can be further improved by using nanodisk codes with disk pairs of different metal compositions and their functionalization with different type and number of chromophores.

Fluorescent barcode nanorods have also been developed using reactive ion etching of fluorescent polymer. Poly (p-phenylene vinylene) film was spin-coated onto silicon substrate. A monolayer of non-close packed silica microspheres arranged as two dimensional arrays was transferred onto the surface of poly (p-phenylene vinylene). The extra poly (p-phenylene vinylene) polymer layer was dissolved using reactive ion etching. Etching process leaves behind array of fluorescent nanorods protected by microspheres. The microspheres were dissolved by hydrofluoric acid treatment to form multi-segmented nanorod arrays on the substrate. Further, the silicon dioxide layer between the substrate and the fluorescent polymer was dissolved and the nanorods were released into the solution (Li et al. 2010). These nanorods could be easily labeled on individual packets.

Invisible nanobarcode tags of 7400 unique barcodes have been reported using chromium grating on the glass substrate. The barcodes were generated by direct write electron beam lithography. These nanobarcodes possessed non-contact remote charge-coupled device array detector based reading of diffraction patterns of tags when exposed to helium-neon laser beam. These can be used as invisible barcodes for product identification (Banu et al. 2006). Further, 68000 tags have been designed by superimposing three different diffraction gratings (Birtwell et al. 2008).

Fluorescent deoxyribonucleic acid dendrimer nanobarcodes have been reported for the detection of *E. coli*, anthrax and tularemia, ebola and severe acute respiratory syndrome pathogens in food and biological samples. Different nanobarcodes were assigned to each microorganism. Nanobarcode detection was performed using fluorescent microscopy, dot blotting and flow cytometry (Li et al. 2005). In a different approach, single strand of deoxyribonucleic acid, i.e. scaffold strand is folded into complex nanorod using many short synthetic staple strands. The staple strands were functionalized with blue, red and green fluorophores. The fluorescent nanostructure was 27 base pair long and was hybridized to 21 base pair staple that extend outwards from the main nanorod body. Variation in the sequence and position of fluorophores on nanorod surface produced 216 distinct barcodes. These barcodes were decoded using total internal reflection fluorescent microscopy (Lin et al. 2012). So, nanoparticles based robust nanobarcode are better than traditional barcodes.

6.5 Electronic Nose and Electronic Tongue for Artificial Smell and Taste Sensing

Artificial detection of smell and taste of food products with human like efficiency helps in producing food of desired quality and taste. Nanoparticles have been explored for designing electronic nose and electronic tongue (Table 6.7).

Table 6.7 Electronic nose and electronic tongue for artificial smell and taste sensing

Type of nanoparticle/ nanobarcode	Method/technique	Analyte	References
Platinum-tin dioxide	Electrical: resistance measurement	Ethanol gas	Ivanov et al. (2004)
Zinc oxide	Electrical: resistance measurement and electrodeless monolithic multichannel quartz crystal microbalance	Ethanol gas and chinese vinegars	Hossain et al. (2005), Zhang et al. (2005, 2006), Mirabbaszadeh and Mehrabian (2012), Ko et al. (2013)
Tungsten oxide-tin oxide	Electrical: resistance measurement	Ethylene gas	Pimtong-Ngam et al. (2007)
Tin dioxide	Linear discriminant analysis and electrical: dynamic headspace extraction analysis	Ethanol gas	Sysoev et al. (2007, 2010), Pan et al. (2010), , Sberveglieri et al. (2012)
Gold	Surface plasmon resonance and indirect competitive immunoassay	Benzaldehyde and olive oil	Gobi et al. (2008), Carlo et al. (2014)
SWCNT	Field-effect transistors	Trimethylamine, amyl butyrate, sucrose, phenylthiocarbamide and propylthiouracil	Kim et al. (2009, 2011), Jin et al. (2012), Lee et al. (2012a), Lim et al. (2013), , Song et al. (2014)
Silver-tin dioxide	Electrical: resistance measurement	Ethylene gas	Baik et al. (2010)
Carboxylated polypyrrole nanotubes	Electrical: sourcemeter	Helional	Lee et al. (2012b)
Gold-Tungsten oxide	Electrical: resistance measurement and continuous flow gas test chamber	Ethanol gas	Stoycheva et al. (2012)
Carbon nanotubes	Field-effect transistor	Hexanal and L-monosodium glutamate	Park et al. (2012), Lee et al. (2015)

(continued)

Table 6.7 (continued)

Type of nanoparticle/ nanobarcode	Method/technique	Analyte	References
Carboxylated polypyrrole nanotube	Field-effect transistor	Phenylthiocarbamide and propylthiouracil	Song et al. (2013)
Silver-tin dioxide	Electrical: resistance measurement	Ethanol gas	Wu et al. (2013b)
Cobalt tetraoxide	Electrical: resistance acquisition system	Ethanol gas	Li et al. (2014)
Molybdenum trioxide	Electrical: resistance measurement	Ethanol gas	Wang et al. (2014)
Magnesium-zinc oxide nanowires	Electrical: resistance acquisition system	Ethanol gas	Kwak et al. (2016)

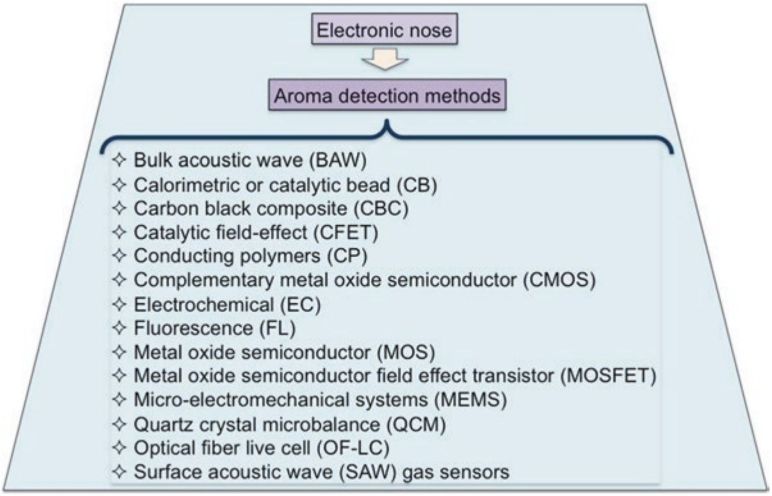

Fig. 6.5 Diagram showing various aroma detection methods used in electronic nose

6.5.1 Electronic Nose

Electronic device that can sense the smell like mammalian olfactory system is called electronic nose. Electronic nose is an instrument derived from aroma-detection techniques. Electric nose mainly consists of gas sensors that senses change in type, quality and quantity of the odor/flavor (Fig. 6.5). Nanoparticles help in better absorption of gas on sensor surface due to more surface area than macroscopic particles (Ranjan et al. 2014; Dasgupta et al. 2015). Different types of principles have been employed to develop diversity of applications of electronic nose in agriculture and food industry (Fig. 6.5). Detailed review of these techniques for application in agriculture and forestry is beyond the scope of chapter and has been discussed by Wilson (2013).

Food industry is major area of electronic nose application. Electronic noses can simultaneously monitor food quality and aromas of multiple food products (Mielle 1996; Baldwin et al. 2011). Electronic nose senses the characteristic volatile organic compounds released from food constituents to ensure good quality, uniformity and consistency of raw material during mixing, cooking and final product during packaging and storage processes (Wilson and Baietto 2009).

Detection of ethylene gas level is useful for monitoring the harvesting, storage and processing of the fruits and vegetables. Excess exposure of ethylene gas deteriorates the quality of fruits and vegetables. Tungsten oxide-tin oxide nanocomposites have been used for the detection of ethylene gas. Ethylene gas interacts with nanocomposite-functionalized electrode. This interaction induces concentration dependent hindrance in the sensors conductivity (Pimtong-Ngam et al. 2007). Silver nanoparticles decorated tin dioxide nanowires based electronic nose has also been employed for ethylene sensing. Tin dioxide nanowires catalyses the oxidation of ethylene. Silver nanoparticles adsorb oxygen and support the oxidation process. The electron generated due to oxidation process resulted in enhancement of sensor current (Baik et al. 2010).

Tungsten oxide and gold nanoparticles has been documented for chemo-resistive ethanol gas sensors. In this gas sensor, the resistance of nanosensor decreased with increase in ethanol gas content. Nanoparticle catalyzes the oxidation of ethanol gas. Ethanol gas oxidation produces electron and thus the resistance of sensor decreases (Sysoev et al. 2007; Stoycheva et al. 2012). Urchin-like magnesium-doped zinc oxide nanowire networks have been reported for the ultrasensitive detection of ethanol gas. Ethanol gas exposure decreases the resistance of nanosensors. Ethanol gas oxidation on the nanosensor surface increased the current flow. This decreased the resistance of nanosensor. The magnesium doping of zinc oxide nanowires significantly enhanced the sensitivity of sensor for ethanol. Magnesium doping lowers the charge carrier concentration of zinc oxide nanowires. Nanomaterial with low charge carrier concentration has better sensing activity (Kwak et al. 2016). Similarly, decrease in nanosensor resistance in presence of ethanol gas has been explored for designing nanoparticle based ethanol gas sensor (Ivanov et al. 2004; Hossain et al. 2005; Pan et al. 2010; Mirabbaszadeh and Mehrabian 2012; Sberveglieri et al. 2012; Wu et al. 2013b; Wang et al. 2014).

In contrast, the resistance of cobalt tetraoxide nanoparticle based sensor increases on exposure to ethanol gas. Flower-like cobalt tetraoxide nanostructures supported on three-dimensional carbon foam were used for sensing ethanol gas. Cobalt tetraoxide nanostructures have holes in the valance bands and thus pose resistance to current flow. Adsorption of ethanol gas generated more holes in the valance band of cobalt tetraoxide nanocomposite. So, the presence of ethanol gas increases the resistance of nanosensor (Li et al. 2014).

Zinc oxide nanorods have been used for designing electrodeless monolithic multichannel quartz crystal microbalance sensors. The electronic nose contains electrodeless quartz crystal plate decorated with zinc oxide nanorods of different sizes. These zinc oxide nanorods act as separate resonators. Each nanorod resonates with different frequencies on exposure to electric field. Ethanol gas thus, changes the resonance frequency pattern of zinc oxide nanorods (Ko et al. 2013). Huang and Wan (2009) has discussed the use of nanoparticles for ethanol gas sensing in detail.

Nanoporous anodic aluminium oxide microcantilever based electronic nose has been designed for sensing volatile organic compounds. Volatile organic compound induces specific molecular vibration transition in the mid infrared region. Change in infrared absorption was easily and specifically quantified using opto-calorimetric spectroscopy techniques (Chae et al. 2015). Single-crystal tin dioxide quasi-1D nanobelt could reliably recognize the aromas of four different beverages namely gluhwein, champagne, vermouth and brandy. Nanobelts contain adsorbed oxygen layers on their surface. Aromatic compounds undergo oxidation by consuming oxygen on the surface of nanobelts. This decreases the diameter of nanobelts. The resistance of nanosensor system increased with decrease in the thickness of nanobelt diameter. These aroma compounds consume different amount of oxygen. Hence, the resistance to nanosensor current depends upon the type of aroma compound (Sysoev et al. 2010).

Gold nanoparticles were used to modify an array of seven quartz crystal microbalance sensors to form electronic nose. So designed nose was used for the detection of extra virgin, virgin and non-edible lampante olive oil. Sensor was also useful for detecting the impurity in the virgin and lampante olive oil samples (Carlo et al. 2014). Likewise, zinc oxide nanoparticles has been used to scrutinize the quality of 17 commercially available Chinese vinegars (Zhang et al. 2006). Manganese dioxide, titanium dioxide and cobalt oxide doped zinc oxide NPs has been used for the identification of five different types of Chinese alcoholic liquors namely, baiyunbian, beijing erguotou, red star erguotou, zhijiangdaqu and jianliliangjiu (Zhang et al. 2005). Surface plasmon resonance-based immunosensor has been designed for the detection of characteristic fragrant compound, benzaldehyde in peach products (Fig. 6.6). Fix amount of anti-benzaldehyde antibodies preferably bind benzaldehyde in the sample as compared to its analog. So, benzaldehyde induces concentration dependent change in the surface plasmon resonance response of nanoparticles (Gobi et al. 2008).

SWCNT field-effect transistor functionalized with human olfactory receptor 2AG1 protein has been reported for odorant sensing. The electronic nose could successfully detect common fruit odorant amylbutyrate in apricot. Odorant binding to receptor induced decrease in transistor current. This nose has better sensitivity than chemical sensors (Kim et al. 2009). Olfactory receptors functionalized carbon nanotubes based transistor has been documented for the selective detection of hexanal. Hexanal is an olfactory indicator of spoiled milk and oxidized food. Hexanal addition induced decrease in the current of transistor (Park et al. 2012).

SWCNT field-effect transistor functionalized with olfactory receptor-derived peptides has been used as electronic nose for the sensing of seafood spoilage. Nose

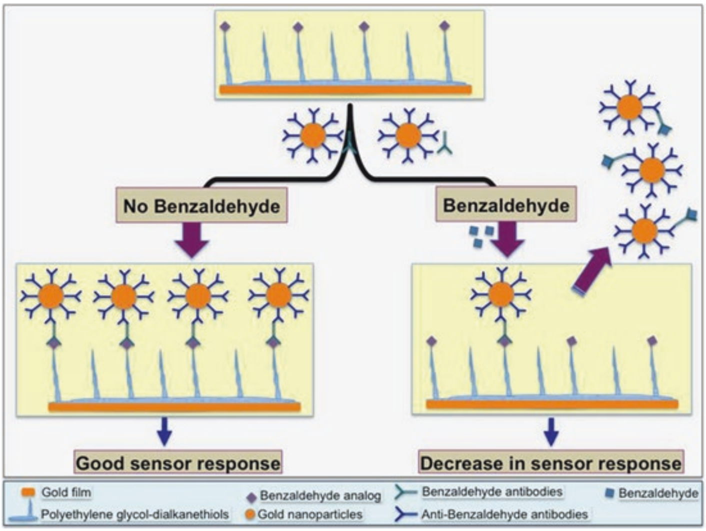

Fig. 6.6 Diagram showing mechanism of gold nanoparticle based sensing of benzaldehyde. Benzaldehyde binding to nanoparticles decreases the sensor response

senses amount of trimethylamine gas generated as a result of seafood spoilage. Sensor could detect trimethylamine up to femtomolar concentration. The olfactory receptor-derived peptide layers selectively adsorb trimethylamine molecules very near to SWCNT channels. Trimethylamine adsorption induced resistance to the flow of current (Lim et al. 2013).

Nanobioelectronic nose has been designed by functionalizing SWCNT and carboxylated polypyrrole nanotubes with human olfactory receptor proteins. The electronic nose could sense gaseous odorants sensitively and selectively up to parts per trillion concentration (Lee et al. 2012a, b). Similarly, nanobioelectronic nose was designed by integrating SWCNT based field-effect transistor with cell-derived nanovesicles containing human olfactory receptors and calcium ion signal pathways. hOR2AG1 receptor functionalized SWCNT acts like human nose to sense amylbutyrate. Amylbutyrate binding to receptor protein triggers enhancement in the calcium ion concentration inside vesicles. Receptor-amylbutyrate binding induced change in the conductance of field-effect transistor. This system has very high sensitivity and could sense amylbutyrate at femtomolar level (Jin et al. 2012).

6.5.2 Electric Tongue

Nanobioelectronic tongue sensor for bitter taste detection has been developed by functionalization of carboxylated polypyrrole nanotube field-effect transistor with human taste receptor protein, hTAS2R38. Interestingly, the nanotongue could

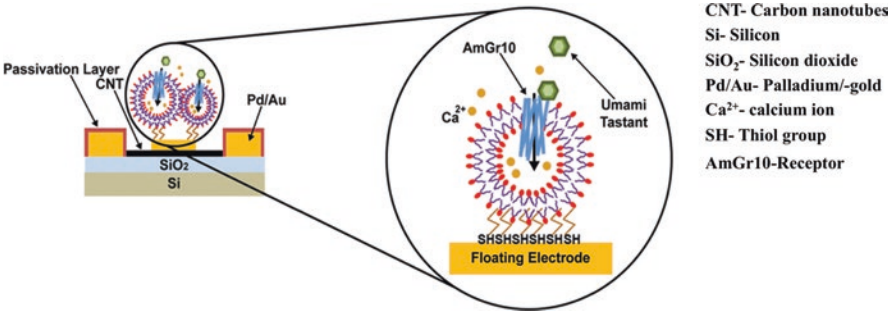

Fig. 6.7 Image showing the basic design of floating electrode-based bioelectronic tongue for umami taste detection. Carbon nanotubes field-effect transistor with floating electrodes hybridized to nanovesicles containing honeybee umami taste receptor, AmGr10 (Figure adapted with permission from (Lee et al. 2015). Copyright (2015) American Chemical Society)

selectively detect target bitterness compounds, phenylthiocarbamide and propylthiouracil with human like efficiency (Song et al. 2013). Similarly, human bitter taste receptor protein was immobilized on SWCNT field-effect transistor to form tasters for bitter taste (Table 6.7). The bioelectronic tongue could discriminate between femtomolar concentration of bitter and non-bitter tastants (Kim et al. 2011). SWCNT field-effect transistor functionalized with nanovesicles containing heterodimeric G-protein-coupled human sweet taste receptors has also been used to develop bioelectronic tongue. Sweeteners bind to the taste receptors and induce current reduction in concentration dependent manner (Song et al. 2014). Floating electrode-based bioelectronic tongue has been designed for the detection of tumami substances. In this study, carbon nanotube field-effect transistor with floating electrodes was hybridized with nanovesicles containing honeybee (*Apis mellifera*) umami taste receptor, gustatory receptor 10 (Fig. 6.7). As the umami taste substance, L-monosodium glutamate binds receptor there is increase in flow of current to electrode. This system was successfully used for the detection of umami taste in chicken soup (Lee et al. 2015).

The nanoparticle based electronic nose and electronic tongue can act as substitute for cell-based assays in order to better understand the mechanism of human taste (Song et al. 2013).

6.6 Conclusion

The unique properties of nanoparticles are responsible for their huge applications. Nanoparticles emerged as useful tool to enhance the sensitivity of traditional food quality detection techniques. Nanosensors have been very useful to enhance the detection limit of existing traditional sensors. Nanosensors ensure fast, reliable and effective detection of microorganisms, toxins and adulterants. It is very useful for the detection of degradable food ingredients like vitamins and antioxidant materials. Nanocomposite materials act as an individual pack quality indicator and smart robust packaging materials. Invisible nanobarcodes protect brands and prevent adulteration. Use of nanoparticles in electronic nose and electronic tongue has lead to develop artificial sensing of smell and taste with human like efficiency. So nanoparticles have huge significance in food industry. Further, advancement in nanotechnology will play a key role in the progression of food industry.

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Chapter 7
From Nutraceuticals to Nanoceuticals

Vandita Kakkar, Nancy Modgill, and Manoj Kumar

Abstract Nanotechnology era comprises an array of food and nutritional supplements referred as nutraceuticals which are transformed to bio-enhanced “Nanoceuticals”. As India’s economy is booming and purchase is on the rise, India’s nutraceuticals market is expected to reach around US$4 billion by 2018.

These products find plentiful space to broaden their therapeutic segment at lab scale, however, their translation to clinics often has resulted in a failure. Latter being assigned to the poor bioavailability of these nutraceuticals, attributed to their poor solubility and permeability, photo-degradation and lower available systemic concentrations. Nanoprocessing of these products may increase their therapeutic value and provide protection from free radical damage. Further, it enhances their antimutagenic potential, provides better neurological functioning, improves endocrine and immunomodulatory functions, in addition to metabolism and digestion, and possesses better anti-aging properties, as a result of enhanced bioavailability. Though no alteration in the chemical structure of the nutrient occurs, however a change in its action for better utilisation and absorption in the body is viewed as a consequence of this translation.

Successful nano-transformation is visioned as a result of approvals from US-FDA which is otherwise sought to be the major milestone for commercialisation of the nano-based product. The Indian market is flooded with a range of nanoceutical products which are delivered via various nanodelivery systems including polymeric and lipidic nanoparticles, micelles, phospholipid complexes and the same is expected to rise in the coming years. As maintaining a good health is our prima-facie responsibility, the shortcomings of the technology must be understood. This book chapter exposes the successful journey for transforming a nutraceutical to nanoceutical and their impact on health of the individual.

Keywords Nutraceutical • Nanoceutical • Nano-encapsulation • Nanoprocessing • Commercialisation • Drug delivery • Food products • Supplements • Approvals • Oversight

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7.1 Introduction

Nanoceuticals are pharmaceuticals or natural supplements, also known as nutraceuticals, which are designed using "nanotechnology". "Nutraceutical", a portmanteau of the words "nutrition" and "pharmaceutical", was coined in 1989 by Stephen L. DeFelice, founder and chairman of the Foundation of Innovation Medicine (Kalra 2003). The term is applied to products that range from isolated nutrients, dietary fibre, prebiotics, probiotics, polyunsaturated fatty acids, antioxidants and other different types of dietary supplements and herbal products, specific diets and processed foods such as cereals, soups, and beverages (Das et al. 2012). Nanotechnology, is referred to as the science of creation and utilization of materials, devices, and systems through the control of matter on the nanometer-length scale. "Nano" means dwarf in Greek, a nanometer is one billionth of a meter i.e. 10^{-9} meter. It was sought to be the province of basic and engineering sciences but now is capturing the world of nutraceuticals, nano biotechnology and nanoceuticals. Although the nanoprocessing does not change the chemical structure of the nutrient, it does change how it acts. Since the first featured article in Food Nanotechnology was published in 2003, there is a growing interest in this exciting research area. Several more featured articles have recently been published to address the potential of food nanotechnology in the areas of food safety/security, functional foods for health promotion applications, nanoscale properties of food materials (Huang et al. 2010), and structural design principles for the delivery of bioactive components (McClements et al. 2009).

Important applications of nanotechnology in food and nutrition refer to the design and development of "novel functional food ingredients" with improved water solubility, thermal stability, oral bioavailability, sensory attributes, and physiological performance. According to the International Food Information Council (IFIC), functional foods are defined as "foods that provide health benefits beyond basic nutrition" (Shibamoto et al. 2008). Nutraceutical compounds such as bioactive proteins are used in functional foods to impart health benefits (Chau et al. 2007).

Driven by the increasing consumer demand for novel food products, as well as increased fortification with healthy food ingredients, the functional food market is expected to reach about $2.5 billion by 2020 (Report 2015; Ranjan et al. 2014), for example, phytochemicals, which are food supplements with health benefits, are commonly used as part of the daily diet. Because of their low solubility in aqueous media, low permeability, rapid metabolism and instability at physiological pH which is a problem encountered with some of the phytochemicals; they are poorly absorbed in the human body (Liu and Feng 2015).Various hurdles faced during the processing, upon delivery and upon storage of these nutraceuticals are depicted in the Fig. 7.1. Encapsulation of phytochemicals leads to enhancement in their bioavailability, in addition to imparting an extended stability to the product (Cushen et al. 2012). Latter helps protecting the drug against various degradative mechanisms (photodegradation, enzymatic degradation).

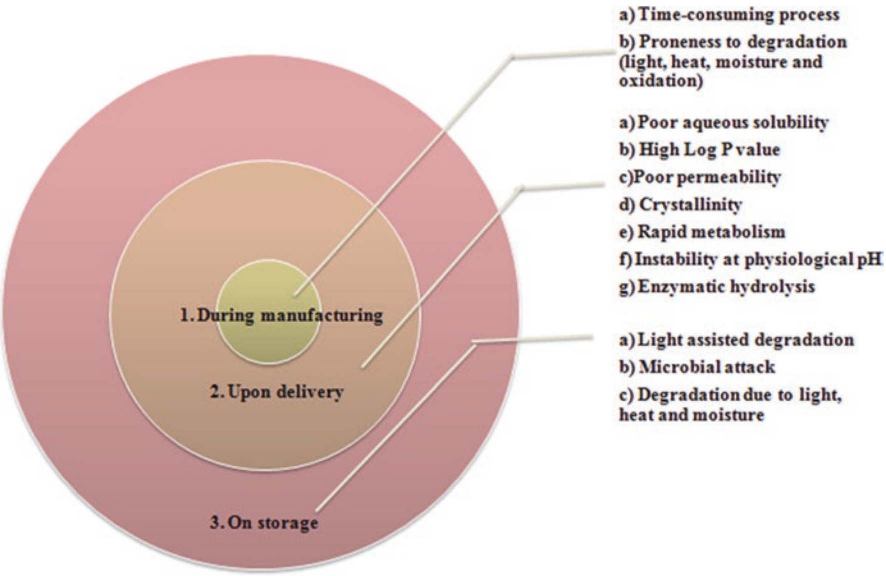

Fig. 7.1 Illustration of problems associated with nutraceutical delivery at three stages of product development (1) manufacturing (2) upon delivery and (3) on storage are clearly depicted in this figure

In the recent years, extensive research to devise nano-encapsulation techniques and specialised polymeric/lipidic materials has been carried out to improve the health promotion properties of different phytochemical based nutraceuticals (Yoshinori et al. 2010). Later improves their systemic availability, delivery properties, solubility and thus their ability to be transferred across intestinal membranes into the blood (Weiss et al. 2006; Shegokar and Muller 2010). Different types of nanoceuticals including the polymeric nanoparticles, solid lipid nanoparticles, magnetic nanoparticles, metal and inorganic nanoparticles, quantum dots, polymeric micelles, phospholipid micelles, colloidal nano-liposomes, nano-emulsions dendrimers polymeric, inorganic, and hybrid nanocarriers have been prepared using techniques like high pressure homogenization, complex coacervation, co-precipitation, salting out technique, solvent displacement method, solvent emulsification-diffusion, supercritical fluid method and self assembly method (Dasgupta et al. 2015; Gunasekaran et al. 2014; Liu and Feng 2015). In addition, nanotechnologies can be utilised to improve the stability of such micronutrients during processing, storage and distribution. These transformed nutraceuticals have nevertheless, reached the market and are grooming to their fullest potential in the hands of the patients/consumers.

Commercial success in this area has been achieved with various nutraceuticals, which include omega-3 fatty acids, and certain beneficial probiotic bacterial species, lycopene, vitamin D_2 and beta-carotene have demonstrated their therapeutic potential in various research studies. Maintaining nutraceuticals in a stable state throughout the production process is invariably challenging. The prospect of the production of nutraceuticals at the nanoscale, which will have increased stability throughout the processing chain, will be of significant interest to food processors trying to maximise nutrient content and hence will ultimately be of benefit to consumers (Dasgupta et al. 2014).

Available literature suggests the tagged uncertainties about nanoceuticals, including the potential for bioaccumulation and potential human health risks (Cushen et al. 2012). While proposed applications of nanotechnologies are wide and varied, developments are met with some caution, while progress may be stifled by lack of governance and potential risks.

7.2 Why "Nutra to Nano"?

"Nanotechnology" which possesses the mysterical powers to revolutionize every field touched by it, is now invading the nutraceutical industry with its great potential (Chellaram et al. 2014).

Converting "nutra to nano" is a logical progression of the technology which is expected to improve the encapsulation and delivery of substances at targeted sites, enhance the bioavailability of phytochemicals, increase the essence of flavors, introduce antibacterial nanoparticles into food, enhance the shelf life of the product, and improve the food storage. (Chellaram et al. 2014). Additionally, the nanoencapsulation of nutraceuticals provides protective barrier against degradation, increased potency, resulting in a controlled release profile of the drug with an improved aqueous stability (Chaudhry et al. 2008a, b; Mozafari et al. 2008). The genesis for this transformation is clearly depicted in Fig. 7.2 in various stages which are involved in developing a product.

Supplements can be easily incorporated by nano-encapsulation techniques for delivering to the target sites effectively (Srinivas et al. 2010). In recent years, the role of food materials has evolved from being solely a source of nutrients to contributing to the health of consumers. When certain nutrients are immobilised in different tailored carriers, the nutrients, such as enzymes, can be resistant to proteases and other denaturing compounds and can have improved stability to pH and temperature changes (Cushen et al. 2012).

Owing to the high bioavailability, potency, and quality of the nanoceuticals for the same price, they are considered to be 'healthier foods'. Hence, smaller amounts are needed during the production which reduces the nutritional ingredient costs per food product, making it more accessible to a wider range of people, thus potentially helping address nutrient shortfalls in developing nations (Buzby 2010).

The nutraceutical industry is ultimately driven by profitability, and keeping in view the gaining consumer acceptability over the value added products (in terms of quality, flavours, textures, safety or reduced cost), it is predicted to grow at an exponential rate. A market research report produced in 2012 projected that the worldwide nutraceuticals market would reach US$250 billion by 2018, defining that

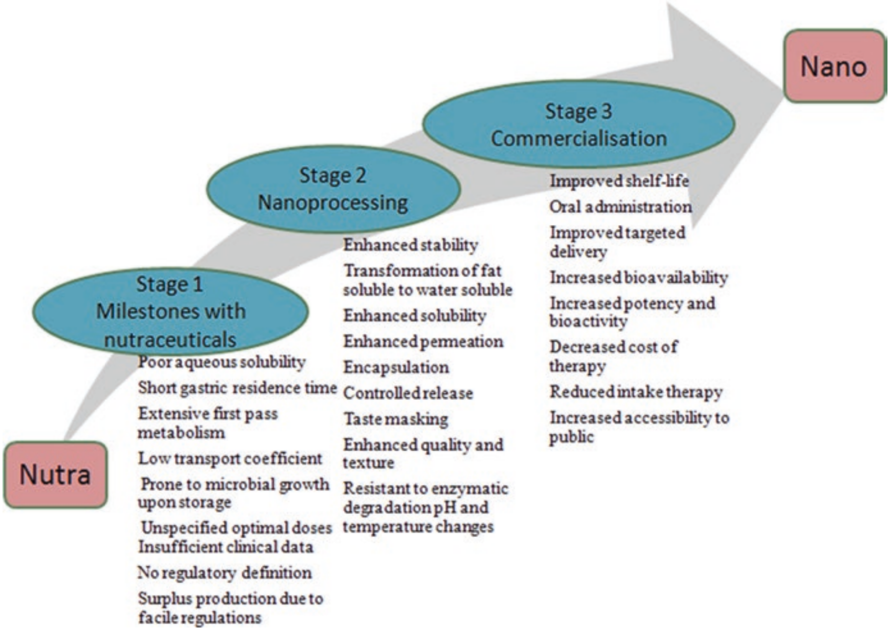

Fig. 7.2 Genesis of transforming nutraceuticals to nanoceuticals in three stages – (1) Milestones with nutraceuticals (2) Nanoprocessing and (3) Commercialization

market as “Dietary Supplements (Vitamins, Minerals, Herbals, Non-Herbals, & Others), and Functional Foods & Beverages” (Smith 2013).

The nanoceuticals thus offer a control and manipulation of properties of substances close to molecular level leading to an increased bioavailability and stability of the product as a result of the various advantages which are clearly depicted in the Fig. 7.2 (stage 2).

7.3 Available Nano-carriers System for Delivering Nutraceuticals

Usefulness of nutraceuticals is ascribed to their ability of imparting the desirable therapeutic benefits with reduced side effects, for the prevention and treatment of various ailments. Their ability to provide protection against a number of diseases including cardiovascular diseases, cancer, diabetes, and even neurodegenerative disorders has been realised by the researchers worldwide. Although the list of nutraceuticals used in the treatment of diseases is quite long, but over the past few years, phytochemicals with potential health and physiological benefits such as polyphenols have been extensively explored using various nanotailoring procedures. These include curcumin, resveratrol, tetrahydrocurcumin, sesamol, hesperidin, quercitin, berberin, blueberry, rutin, and carotenoids like beta-carotene present in yellow, orange, and green vegetables and fruits. All such "nanoceuticals" as the term applies have attracted researchers as well as consumers with their ability to prevent and treat a number of diseases like cancers (Kakkar et al. 2012), cardiovascular disorders, emotional and central cognitive derangements (Kakkar et al. 2011) and even neurodegenerative disorders like Alzheimer's disease (Kakkar et al. 2013a, b) and also their beneficial effects in improving the immunity.

However, the low bioavailability associated with majority of the phytochemicals assigned to their poor solubility in the aqueous media and gastrointestinal fluids, rapid metabolism, poor permeability, instability at physiological pH, enzymatic and light assisted degradation lead to their incomplete absorption resulting in their diminished or no biological activity. Latter is of concern to the scientists today. In order to address this issue, principles of nanotechnology have been utilized for the efficient delivery of these nutraceuticals with the aim to enhance their biological activity. A number of formulation approaches like nanoemulsions, micelles, nanoparticles, nanocapsules, nanocochleates, nanocrystals, etc. have been utilized for the efficient delivery of the encapsulated nutraceutical. The developed nanoformulations provide a targeted delivery of the encapsulated phytochemical as well as its sustained release from the nanoformulation besides improving its bioavailability and hence therapeutic efficacy.

A good example to illustrate this is the tremendous improvement in the solubility and hence bioavailability of curcumin. Curcumin the "Indian gold" is a nutraceutical with anticancer potential which has been proved by various animal and cell culture models, by formulation of different nanoformulations like polymeric nanoparticles, lipidic nanoparticles (Kakkar et al. 2013a, b; Kakkar et al. 2012), nanoemulsions, micelles, phospholipid complexes and liposomes. Our experience with this challenging molecule is clearly reflected by the pharmacodynamic studies of the prepared curcumin solid lipid nanoparticles in various animal models for cerebral ischemia (Kakkar et al. 2013a, b), Alzheimer's disease (Kakkar and Kaur 2011), depression (Kakkar and Kaur 2012), and in *in vitro* anti-cancer cell line (Bhushan et al. 2013). Another example can be traced from a Chinese drug, Cuscuta chinensis (C. chinensis), which contains flavonoids and lignins. It has poor aqueous solubility and poor absorption when administered orally. The nano sized C. chinensis were prepared by a nanosuspension method and were found to have hepatoprotective and antioxidant effects after oral administration (Gunasekaran et al. 2014). An oral formulation of epigallocatechin-3-gallate, a polyphenol found in green tea was synthesised by encapsulating it in a formulation of chitosan nanoparticles and its antitumor efficacy was assessed in subcutaneously implanted 22Rν1 tumor xenografts in athymic nude mice. Successful inhibition of prostate cancer cell growth was observed in a xenograft model (Khan et al. 2014). In another study, the stability and the release of resveratrol, a natural polyphenol with anti-tumour activities, was improved by preparing reseveratrol-loaded polyethylene glycol–polylactic acid polymer nanoparticles using the solvent evaporation method. Authors reported a successful suppression of glucose metabolism and tumor growth both in *in vitro* and *in vivo* studies and concluding it to be an effective method in cancer delivery (Jung et al. 2015). Another study, reported a method for preparing a solid self-emulsifying drug delivery system (SMEDDS) for the transportation of rutin, a polyphenolic compound with anti-allergic, anti-inflammatory, anti-tumour, anti-bacterial activities. Owing to its improved rheology and fast release it could be delivered orally as a nutritional supplement (Kamel and Basha 2013). The oral bioavailability of quercetin, a polyphenol which has anti-inflammatory, antioxidant, antiviral, anti-carcinogenic and cardioprotective properties has also been improved by preparing its fast dissolving nanocrystals by high-pressure homogenization technique using maltodextrin (Lai et al. 2015).

Although, success in improving the bioavailability and therapeutic potential of nano processed phytochemicals has been achieved *in vitro* and to some extent in various *in vivo* studies, however extensive studies in animal models still need to be done to prove their efficacy. Furthermore, risk assessment of precipitating a toxicity as a result of enhanced bioavailability and proving their safety to the human body as well as to the environment must be analysed.

7.4 Rising Market Demand for Nanoceuticals: Expectations and Concerns

Even with the lack of scientific evidence regarding safety or efficacy, it has been estimated that more than fifty nanoceuticals have reached the market. Also, the number of the nanotechnology-based food and beverage packaging market has reached $7.3 billion by 2014 (Duvall 2012), according to the Project on Emerging Nanotechnologies' inventory of nanotechnology-based consumer products.

Claims prophesied by the manufacturers of nanoceuticals include (a) transformation of fat-soluble nutrients into water-soluble ones, (b) complete and uniform nutrient absorption, (c) increased permeability of supplements across biological membranes, (d) lowered risk of serious side effects and (d) enhanced effect with lower dose. The unprecedented rise in the nutraceutical sector may be attributed to the below listed features.

As a significant strata of the Indian population of 1.2 billion belongs to the middle class, their focus on maintaining a good health and appearance, has empowered the development of nutraceuticals sector at a fast pace. According to a report on Nutraceuticals Market in India, rising number of people in the country are purchasing products including supplements, beverages and food, designed to boost their health, prevent disease, enhance alertness and stamina (Report 2011). The industry is anticipated to grow around 20 percent and reach USD 6.1 billion by 2019–2020. Though usefulness of these products has been realised by the people, however, they are still in an embryonic stage, as far as their safety is concerned. Another element driving demand for nutraceuticals in India is soaring obesity rates as people adopt more sedentary lives and consume greater amounts of fast foods, driving them to try and counter this by taking supplements and other nutraceuticals.

In addition to the above, the oversight of the FDA regulators is a major concern. Like all the dietary supplements, nanoceuticals are unregulated and can be introduced to the market with little or no evidence of safety or efficacy. The FDA claims to regulate products, not technologies, further it is unable to address the whole range of potential risks, during the life cycle of the nanotechnological processing, which involves, release of waste in the environment during its production and use in addition to their direct effects on human body (FDA 2014). It expects many nanotechnology food and supplement products to come under the jurisdiction of the Office of Combination Products. Yet the Institute of Food Science and Technology reports that nanoparticles should be treated as potentially harmful until testing proves otherwise. The 2007 FDA Nanotechnology Task Force made several considerations regarding the FDA oversight. As a result, FDA reorganized its offices and opened the Office of Food Additive Safety to regulate the approval for nanoceuticals, dietary supplements, other nutrients and color additives (Buzby 2010). Increasing the bioavailability of nutrients and phytochemicals may be promising but is also potentially dangerous.

While upper limits are established for most vitamins and minerals, there are no upper limits set for phytochemicals. As nanoceuticals can help bypass typical protective barriers in the body and deliver quantities of biochemicals that the body would not naturally encounter. This makes the introduction of nanoceuticals potentially dangerous, especially when the government does not regulate them effectively.

Nanoceutical market is a mass market which addresses healthcare, thus claiming their extent of safety on broad terms would be an irrelevant statement. The Australian government examined that the “bioaccumulation and biopersistence are common characteristics of nanoparticles” and that there exists “sufficient uncertainty in the human health effects of all nanoparticles, following either short term or long term exposure”(Bruschi and Thomas 2006).

Regulatory bodies hold different views regarding nanotechnology. One perspective is that a governing system is required which functions across the entire life cycle of the nanoceuticals with greater focus on managing the steps with greatest risks. While, another perspective is, to switch to an established regulatory system similar to the one in practise for other divisions. Owing to the huge applications put forth to FDA for a range of nanotechnology based products, it is owesome for the regulators to direct the innovators with a justified decision (FDA 2014).

The FDA infact lacks the scientific expertise and resources to effectively regulate nanomaterials in supplements and to accumulate data in this regard. According to William Schultz and Lisa Barclay, authors of ‘*A Hard Pill to Swallow: Barriers to Effective FDA Regulation of Nanotechnology-Based Dietary Supplements*’, there are several problems the FDA needs to address (Schultz and Barclay 2009). For one, the FDA does not have the capacity to identify nano-based dietary supplements that are being developed and marketed. Latter requires the manufacturers to submit the premarket notification process for new dietary ingredients by providing the safety data before launching their product in the market. The nanoceuticals do not however fall in this category and hence are marketed without any concrete governing regulation and are subjected to less stringency by the FDA regulatory authority (Buzby 2010). Additionally, the scientific evidence of duration of the clinical studies, validation of the biological markers, dose response curves to define the efficient dosage and the adverse effects are not well established (UBIC 2011). Designing a testing procedure with better predictive and risk assessment capacity on these products, their physicochemical characterization, biological evaluation, and a need for new expertise to ensure the development of nanoceuticals, is presently, the main concern of FDA (Kaur et al. 2014).

Recommendations for regulating the safety of nanoceuticals have been made (Schultz and Barclay 2009). These include:

- Firstly, there must be an increased regulatory authority of FDA over dietary supplements containing engineered nanoparticles.
- Secondly, there is a need for a widely accepted definition of nanotechnology, such that a clear picture of the labelling instructions can be unveiled on the label. Latter however, may infuse doubts relating to the safety of the nano-products (Buzby 2010). This would in turn be a profitable business deal for the manufacturers and an oversight for the regulators. The need of the hour is to empower FDA for gaining recent information on the nanoceuticals labelling requirement in the market, in addition to the safety testing for the product.
- Thirdly, the strict regulations must be imposed by the FDA for such nutraceutical products.

Concrete steps ought to be taken by the international regulatory bodies to examine the impact of nanotechnology on humans and environment by carrying out the risk assessment studies. These studies could be based upon the life cycle assessment or systems approach to environmental protection incorporating the processing, manufacturing, distribution, use, and, possibly, recovery management of the nanoceuticals. Market value of the nanoceuticals is manifested by the response of the public regarding the product. Several factors like the perceived risks and benefits, quality, authenticity of the product, price, and general attitudes, values and cultural norms play an important role in the eyes of the consumers to accept a new food technology. It has also been observed that nanoceutical market is consumer driven and companies must carefully consider their demand in the positioning of their products (OECD 2007). The consumers are more reluctant to buy food that incorporates nanotechnology i.e. nanoceuticals than using a nanoprocessed packaging material. Some sociologists believe that consumers prefer preserving the naturality of the food and their suspicion increases with the decreased proximity between the natural and processed food. It, therefore becomes imperative for the regulatory agencies to keep up the trust of the consumers and the government while carrying out the risk assessment studies for nanoceuticals and their acceptance (Buzby 2010).

7.5 A Market Review

Nanotechnology has already opened up a way for a multibillion dollar global industry in recent years. The market impact of nanotechnology is widely expected to reach 1 trillion US$ by 2015, with around 2 million workers (Boxall et al. 2007). Whilst the majority of manufacturing and use of nano-scale materials occurs in the United States, the European Union (EU), with its 30% global share of this sector, is not lagging far behind. Within the European Union, the UK accounts for nearly a third of the sector (Chaudhry et al. 2008a, b). A variety of consumer products that contain nanomaterials are already available in the UK and the EU. A scoping study into the manufacture and use of nanomaterials in the UK, Central Science Laboratory, York estimates of the current global market size and number of companies involved in the nanofood sector are varied because of the scarcity of exact information due to commercial and environmental sensitivities (Chaudhry et al. 2008a, b). The exponential growth of the nanoceuticals points towards the consumer acceptability and their concern for keeping abreast with the novel technologies for improving their health. It has been suggested that the number of companies undertaking research or using nanotechnology for food or food packaging applications may be between 200 and 400 according to a report published in August 2006 in Cientifica 'Nanotechnologies in the Food Industry'. These also include some major international food industries and beverage firms. It is also widely anticipated that there would be an unprecedented increase in the companies venturing into nanotechnology business in the near future. The European Union, United States, Japan and China are the world leaders for the food and agriculture applications. US is the largest nutraceutical market owing to its cultural as well as regulating factors. US consumers largely consume food supplements, and their regulation and new product commercialization are not stringent. In the USA, the companies like Hansen, Naked Juice, Jamba Juice and Snapple, are utilising a whole range of nutraceuticals such as ginseng, gingko, omega3, for teas and juices. Products containing alcoholic beverages and the flavonoids and polyphenols are also hitting the market. Hence, many large food corporations are at the forefront of nutrition research, and are endeavoring to boost the marketing of nanoceuticals. Japan was the first country to recognize and regulate functional foods and introduced Food for Specific Health Use (FOSHU) in the early 1980s. As a large strata of population in Japan belong to an elderly class with a taste for traditional phytotherapy, they have gained an expertise in bioproduct and have a flexible regulatory requirement. Today, it owes a market with $12 billions for both nutraceuticals and food supplements. While in Europe, with stringent regulations, the number of products which are commercially successful are just meagre. The Project on Emerging Nanotechnologies (PEN) by the Woodrow Wilson International Center for Scholars established in April 2005, compiles and publishes an online inventory of commercially available nanotechnology-based consumer products worldwide and 43 supplements comprising 57.3 % items in this list were attributed to the food supplements (Maynard and Michelson 2005). Table 7.1 enlists the nanoceuticals product commercialised in the last decade with their manufacturer and therapeutic essence.

Table 7.1 List of commercialised nanobased food products

Name of the product	Type/constituents	Manufacturers	Key points
EP2235158B1 (Chung et al. 2013)	Triple-coated lactic acid bacteria with polysaccharides and nanoparticles	Cell Biotech Co., Ltd. Gyeonggi-do 415-872, South Korea	Better acid resistance, and bile resistance; enhanced stability
Nanotea (Sekhon 2010)	Tea leaves enriched in Selenium	Shenzhen Become Industry Trading Co. Guangdong, China	Employs ball milling nanotechnology (Powell et al. 2010)
Fortified Fruit Juice (Sekhon 2010)	–	High Vive.com, USA	–
Nanoceuticals Slim Shake (Sekhon 2010)	Nanoencapsulation of cocoa (Powell et al. 2010)	RBC Lifesciences, Irving, USA	Enhanced flavour
NanoSlim beverage (Lee 2014)	–	NanoSlim	–
Oat Nutritional Drink (Lee 2014)	–	Toddler Health, Los Angeles, USA	Enhanced flavour
'Daily Vitamin Boost' fortified Jamba juice (Sekhon 2010)	22 essential vitamins and minerals offered daily	Hawaii, USA	–
Canola Active Oil (Tiju and Morrison 2006)	Nano-sized Self-assembled Liquid Structures (NSSL) based nano- micellar carrier system (Chaudhry et al. 2008a, b)	Shemen, Haifa, Israel	Improved penetration of vitamins, minerals and phytochemicals. Reduction in cholesterol intake by 14 % is claimed (Tiju and Morrison 2006)
NovaSol Sustain beverages (Silva et al. 2012)	(coenzyme Q10, DL-a-tocopherol acetate, vitamins A, D, D3, E, and K and omega three fatty acids)	German based company Aquanova (Darmstadt, Germany).	CoQ$_{10}$ burns fat and alpha-lipoic acid improves satiety (Tiju and Morrison 2006)
SoluE (Tiju and Morrison 2006)	Vitamin E preparation	Aquanova	No clouding effect. Protection against acidic environment of stomach.
SoluC (Tiju and Morrison 2006)	Vitamin C preparation	Aquanova	Protection against acidic environment of stomach.
Megace® ES (MA-ES)	Nanocrystal dispersion with micronized particles (Femia and Goyette 2005)	Par Pharmaceutical, Inc. Par licensed the Megace® name from Bristol-Myers Squibb Company, New York, USA	Appetite stimulant in case of cachexia.

(continued)

Table 7.1 (continued)

Name of the product	Type/constituents	Manufacturers	Key points
Beverages by Nutralease (Silva et al. 2012)	Nanoemulsions of encapsulated functional compounds such as coenzyme Q10, lycopene, lutein, ß-carotene, omega-3, vitamins A, D3 and E, phytosterols and isoflavones(Silva et al. 2012)	Nutralease Ltd., Israel	Nano-sized Self-assembled Liquid Structures (NSSL) technology allows drugs to enter from gut to blood and hence delivers nutrients in nanosized particles to cells.
Tip-top bread (Tiju and Morrison 2006)	Nanocapsules incorporating tuna fish oil (a source of omega 3 fatty acids)	George Weston Foods, Enfield, Western Australia	The nanocapsules break upon reaching the stomach, masking unpleasant taste of the fish oil in the mouth.
OilFresh™ 1000 and 3000 series (Report 2006)	Nanoceramic product	The US based Oilfresh Corporation	Large surface area, reduced oxidation, suppresses oil breakdown process which reduces the oil usage in fast food, increases its span, maintains consistency in the quality. (Report 2006)
Nanoceuticals™ Spirulina Nanoclusters (Schultz and Barclay 2009)	Nanosized powders	RBC Life Sciences Inc. USA	A delivery system for enhanced nutritive value with increased absorption.
Bioral (Peters et al. 2011)	Nanocochleate containing Calcium ions in a GRAS phosphatidylserine carrier derived from soya bean	BioDelivery Sciences International.	A protective delivery system for micronutrients and antioxidants against enzymatic degradation

7.6 Conclusion

Transforming nutraceutical to the nano form has been viewed as a foundation stone of the upcoming manufacturer-consumer relationship. The nanoceuticals with their captivating property as a consequence of enhanced bioavailability offer unmatchable properties, to the nutraceutical per se. Latter is a major contributing factor which has led to the oversight by the regulators which have given a green signal to ample products which are in the market for consumer use. The regulatory agencies ought to take concrete measures in order to establish a standardised international board which will set guidelines, develop new policies and make reforms to normalise the safety assessment procedure which governs the approval of the nanoceutical products and regulate the products entering into the market. However, in order to accomplish the commercialisation process successfully, the consumers also must be advocated about the benefit over risk of these nanoceuticals. The motive should not only be considering the merits and the de-merits but also using the tools and the technology in an efficient manner and preventing their misuse. Therefore, a harmonious effort by the regulatory agencies, the manufacturers and the consumers can aid in achieving a sustainable socio-economic-environmental development of this unique technology and help in revolutionising the nutraceutical sector.

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Chapter 8
Selective Removal of Nitrate and Phosphate from Wastewater Using Nanoscale Materials

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Abstract Excessive nitrogen (N) and phosphorous (P) release into runoff from human activities is a major cause of eutrophication, which degrades freshwater and ecosystems. Phosphate and nitrate pollutants can be removed by chemical precipitation, biological treatment, membrane processes, electrolytic treatment, ion-exchange and adsorption process to remove these pollutants from water sources effectively. Adsorption is a cost-effective solution for efficient nitrate and phosphate ions removal. In this review various nanoscale adsorbents such as zero-valent metal, metal oxides, functionalized materials and carbon-based materials are surveyed. Their adsorption capacities under various conditions are compared.

Keywords Eutrophication • Nanomaterials • Nitrate • Phosphate • Composite materials

Abbreviations

BOD	Biochemical Oxygen Demand
C-cloth	Carbon cloth
CNT	Carbon nanotube
COD	Chemical Oxygen Demand
DNA	Deoxyribonucleic acid
EDTA	Ethylenediamine tetracetic acid

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G-nZVI	Graphene-supported nanoscale zero-valent iron
HZO	Nano-hydrous zirconium oxide
IEP	iso electric point
La-ZFA	Lanthanum hydroxide-Zeolite
MZVI	micro-ZVI
NOAA	National oceanic and atmospheric association
nZVI	Nanoscale zero-valent iron
OMM	Ordered mesoporous materials
ppm	Parts per million
RO	Reverse osmosis
SBA	Santa Barbara Amorphous
TDS	Total dissolved solids
USEPA	U.S. Environmental Protection Agency
WHO	World health organization

8.1 Introduction

Water played a crucial part in the origin of life and it still has an essential role in maintaining plant and animal life. Plants depend on water for the transfer of nutrients and for photosynthesis. Nearly all the processes essential for life depend on reactions that take place in an aqueous solution, be it the division of DNA in a cell, the digestion of food stuffs in the stomach or the transport of oxygen around the body (Wardlaw 2012; Nandita et al. 2015; Shivendu et al. 2014). Given an importance of water, it is not surprising that human can survive very much longer without food that they can't without water. Historically, availability of water supplies has determined where villages, towns and cities are located. Nomadic peoples and animals, may travel hundreds of miles over the course of a year following the seasonal variation in rainfall. A lack of good quality drinking water and water for sanitation brings deadly diseases such as typhoid (Schlipkoter and Flahault 2010). All these factors and many more, make water a material of great importance. The starting point of water pollution occurs when rain drops fall through the atmosphere they dissolve small quantities of gases in the atmosphere. Where there is little air pollution, the gases are mainly nitrogen, oxygen and a little carbon dioxide does make the water very slightly acidic owing to the production of weak carbonic acid. Rain falling in a thunderstorm is more acidic than normal. The energy of the lightning is sufficient to dissociate nitrogen molecules, which then combine with oxygen to give oxides such as nitrogen dioxide (Schumann and Huntrieser 2007). Once rain water contact with land surface, water pollution begins slowly depending upon distanced travelled by water, there may be following types of impurities present in the water (APHA 1985):

(i) Dissolved impurities: The following impurities may be present in the water in the dissolved form:

Table 8.1 Water quality parameters

Physical parameters	Chemical parameters	Biological parameters
Colour	Dissolved oxygen	Bacteria (pathogenic)
Odour	Biochemical oxygen demand	Coliforms and other bacteria
Turbidity	Chemical oxygen demand	Algae
Conductivity	pH, alkalinity	Viruses
Solids	Ammonia, nitrates, nitrites, sulphates, phosphates chlorides, silica, calcium, magnesium, hardness, sodium, potassium, iron, heavy metals, detergents, and pesticides	

- Inorganic salts: cations like Ca^{2+}, Mg^{+2}, Na^{+}, K^{+}, Fe^{+2}, Cu^{+2}, Al^{+3} and anions like Cl^{-}, SO_4^{2-}, HCO_3^{-}, NO_3^{-}, PO_4^{3-} and sometimes F^{-} and NO_2^{-}
- Organic salts: drugs and dyes
- Dissolved gases: O_2, CO_2, NOx and SOx and sometimes NH_3 and H_2S
- Toxic elements: Like Hg^{2+}, As^{5+}, Cr^{6+}, Pb^{2+}, Cd^{2+} etc

(ii) Colloidal impurities: clay, silica, $Al(OH)_3$, $Fe(OH)_3$, humic acids, etc.
(iii) Suspended impurities: Inorganic matters (clay and sand) while organic matters (oils globules, vegetables and animal matter)
(iv) Biological impurities: Bacteria and micro-organism (virus, algae, fungi and diatoms)

8.1.1 Water Quality

The treatment of water in order to make it suitable for drinking, domestic or industrial use includes a physical, chemical and biological methods which change an initial composition of water. Water treatment involves not only purification and removal of various unwanted and harmful impurities, but also improvement of the natural properties of water by adding certain deficient ingredients. Water quality parameters based on the present-day standards and guidelines are presented to assist in the establishment of water system performance goals for any plant. The water quality parameters are generally divided into three categories like physical, chemical and biological (Pfafflin and Ziegler 2006). These parameters are briefly summarized in Table 8.1.

The standards for drinking water quality are typically set by governments or by international standards (WHO 1997). These standards usually include minimum and maximum concentrations of contaminants, depending on the intended purpose of water use. Visual inspection cannot determine if water is of appropriate quality. Simple procedures such as boiling or the use of a household activated carbon filter are not sufficient for treating all the possible contaminants that may be present in water from an unknown source. Even natural spring water considered safe for all practical purposes in the nineteenth century must now be tested before determining what kind of treatment, if any, is needed. Chemical and microbiological analysis, while expensive, are the only way to obtain the information necessary for deciding on the appropriate method of purification (Droste 1998).

8.1.2 Nitrate and Phosphate Pollution

The nitrate and phosphate substances are among the most problematic pollutants which significantly affecting the surface and groundwater all around the world. However, the nitrate and the phosphate pollution has been neglected by many countries. The rapid development of industrial and agricultural activities have take over the human awareness on the effects of nutrients pollution to us and to the environments. Considering the bad effects of phosphate and nitrate pollution, WHO permits 5 mg/L as the maximum level of phosphate whereas for nitrate not more than 10 mg/L that is safe in drinking water (WHO 1985). Common causes of phosphate toxicity in humans include impaired renal function, rhabdomyolysis and tumourlysis syndrome. In addition, exogenous phosphate toxicity is also documented in patients with Hirschsprung disease when exposed to hypertonic phosphate enemas (Razzaque 2011). When human consume high concentration of nitrate through contaminated drinking water, there is high risks of being infected by diseases like methaemoglobinemia, gastric cancer and non-Hodgkin's lymphoma (APHA 1998; Rademacher et al. 1992). Besides, the long term exposure to nitrates and nitrites at level above maximum contamination level will cause diseases like diuresis, increased starchy deposits and hemorrhaging of the spleen (EPA 1990). Hence, the removal of nitrate and phosphate from wastewater prior to discharge is now necessary. Several methods are being used to remove nitrate and phosphate ions. The present review articles deals with the current techniques for the nitrate and phosphate ions removal from waste water (Fig. 8.1).

8.2 Methods of Nitrate and Phosphate Removal

Traditional methods for nitrogen removal from waste water are biological denitrification processes, ion exchange, reverse osmosis, electrodialysis, and chemical denitrification. Among these methods, the first four methods have been applied in industry. Each of these technologies has its own strengths and drawbacks and their feasibility depends on the various factors such as cost, water quality improvement, residuals handling, and post-treatment requirements.

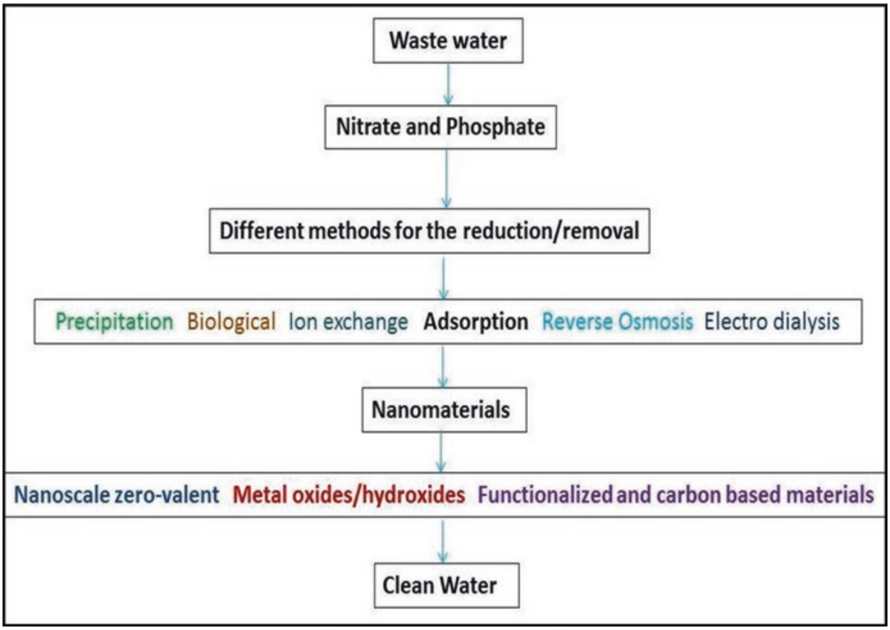

Fig. 8.1 Treatment technologies for the reduction of nitrates and phosphates in wastewater

8.2.1 Biological Denitrification Process

In this process, nitrate is converted to nitrogen gas by denitrifying bacteria in the absence of oxygen ($NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$). In order to satisfy the growth and energy requirements of the bacteria, methanol in excess of 25–35 % must be added as a source of carbon. The removal efficiency ranges from 60 to 95 %. The major advantage to anaerobic denitrification is that there are no waste products requiring disposal, produces a non-toxic by product (N_2), suitable for large applications, can handle high concentrations, and destructive method. The nitrate removal from wastewater by the biological denitrification technology using immobilized *Psuedomonas Stutzeri* bacteria in a fluidized bed bio reactor with different initial nitrate concentrations (150, 180 and 200 ppm) and found that the nitrogen removal efficiency achieved was highest (96 %) with methanol as carbon source, followed by ethanol (77 %) and methane (70 %) during the period 6–8 h (Srinu and Setty 2011). The influence of low-intensity ultrasound to biological denitrification for nitrate removal from synthetic wastewater (Xie and Liu 2010). They used ethanol as the carbon source and showed that the ultrasonic intensity of 0.2 Wcm^{-2} and irradiation time of 10 min may be the most effective and economical ultrasonic parameters to enhance the efficiency of biological nitrogen removal processes. Some of the disadvantages of this method like electron donor and carbon source required, requires downstream treatment (e.g., ozonation), high-maintenance, long start-up times, pH temperature sensitive and membrane fouling.

8.2.2 Ion Exchange Process

In the Ion exchange process (IEP), wastewater is passed through a media bed which removes both anionic phosphorus and anionic nitrogen ions and replaces them with another ion from the media. The exhausted resin will be regenerated using a concentrated solution of brine. Besides, this technique found to be stable, quick removal, easily automated, cost-effective, low maintenance and non-destructive. Difficulties in the process may be caused by fouling of the IE resin due to organic backbone and reduction in the exchange capacity due to sulphates and other ions. The efficiency and cost of nitrogen and phosphorus removal by IE depends largely on the degree of pre-treatment and the quality of the water to be treated. Removal of nitrogen and phosphorus contents ranges from between 80 to 92 % using strong base anion resins (Amberlite IRA-410). Several resins have been tested for nitrate removal from ground water such as strong base anion exchange resin Purolite A 520E with column (Samatya et al. 2006). The total capacity was calculated to be 157 mg NO_3^- per gram resin and the column utilization efficiency was about 81 %. They used 0.6 M NaCl to elute nitrate loaded on resin and elution efficiency was about 96 %. Equilibrium and kinetic parameters for the removal of nitrate ions from aqueous solutions on Amberlite IRA 400 resin and maximum adsorption capacity was found to be 769 mg NO_3^- per gram at 25 °C (Chabani et al. 2006).

8.2.3 Reverse Osmosis

In reverse osmosis (RO), water begins to flow in the reverse direction with the application of pressure (750 psi) higher than the value of osmotic pressure. The pressure required to force the permeation through the membrane is dictated by the osmotic pressure of the feed stream. Membranes are generally made of materials such as cellulose acetate, polyamides and composite materials. In actual practice the process has been beset with difficulties primarily due to membrane fouling, expensive energy, large capital costs and requires treatment or disposal of concentrate. In addition, some nitrate and phosphate ions escape through the membrane (efficiency about 65–95 %). Advantages of this technique are good for waters with high TDS content, no by products, non-destructive**.** A comparison between three technologies RO, IE and biological process for nitrate removal has been studied (Darbi et al. 2003). They showed that the lowest nitrate removal efficiency was obtained with RO (85 %) with compared to 90 and 96 % for IE and biological process, respectively. The RO could be very effectively applied for water desalination and water denitrification in a rural area (Schoeman and Steyn 2003). They showed that the nitrate-nitrogen was reduced from 42.5 mg/L in the RO feed to only 0.9 mg/L in the RO product water (98 % removal). Removal of ammonium and nitrate from mine water by using RO and the retention of nitrate was reported to be more than 90 % (Hayrynen et al. 2009) during the concentration. In another study (Richards et al.

2010) carried out to evaluate the impact of pH on retention of nitrate by reverse osmosis (RO) and reported that the nitrate retention depended on membrane types, and was mostly pH independent.

8.2.4 Electrodialysis

Like reverse osmosis, electrodialysis (ED) is a non-selective demineralization process which removes all ions which would include the nitrate and phosphate ions. ED is accomplished by making cation and anion from aqueous solutions pass through IE selective membranes using the driving force of an electric field. When electric current is applied, the cations pass through the cation-exchanging membranes in one direction and the anions pass through the anion-exchanging membranes in the other direction (Hell et al. 1998). Disadvantages in the operation of this process include membrane clogging and precipitation of low-solubility salts of the membrane. Acidification of the water and removal of some of the solids prior to treatment has been effective in minimizing these problems and it adds to the cost. Removal efficiency ranges from between 30 to 50 % (for nitrogen). Removal of nitrate in Moroccan groundwater carried out by ED using different types of anion exchange membranes with one type of cation exchange membrane to treat water containing 113 mg/L of nitrate (El Midaoui et al. 2001 and 2002). They found that the content of nitrate was reduced to 30 mg/L after 1 h of ED operation. Considering the effect of pH, the study showed 3 and 5 were the most effective operating condition for the separation of nitrate from aqueous solutions using ED and the concentration of nitrate was reported to decrease from 173.8 mg/L to 4–5 mg/L after 42 min of operation (Abou-Shady et al. 2012).

8.2.5 Chemical Precipitation

Chemical precipitation is a flexible technology allowing for application of the metal salts at several stages during wastewater treatment (EPA 2000; Jenkins et al. 1971; Jiang and Graham 1998). Precipitation of phosphorus in wastewater may be accomplished by the addition of such coagulants as lime, alum, ferric salts and polyelectrolytes either in the primary or secondary state of treatment, or as a separate operation in tertiary treatment. In general, large doses in the order of 200–400 ppm of coagulant are required. However, subsequent coagulation and sedimentation may reduce total phosphates to as low as 0.5 ppm, as in the case of lime. Doses of alum of about 100–200 ppm have reportedly reduced orthophosphates to less than 1.0 ppm. Phosphorus removal by chemical coagulation generally is efficient with removals in the order of 90–95 % reported. Additional benefits are gained in the process by a reduction in BOD to a value of less than 1.0 ppm. Both installation and chemical costs are high, however, and the sludges produced are both voluminous and calculations of accurate dosages of chemicals are impossible because of changing levels of alkalinity, different competitive reactions and other factors.

8.3 Adsorption

Adsorption was first observed by C.W. Scheele in 1773 for gases, followed by Lowitz's experiments in 1785 for solution (Kraemer 1930). Adsorption is the accumulation of a substance at a surface or the interface between two phases. It is a surface phenomenon. The adsorption process can occur at any interface such as liquid-liquid, gas-solid, gas-liquid, or liquid-solid, but liquid-solid interfaces of special interest from the water and wastewater treatment point of view. Basically, it is a surface phenomenon and adsorption takes place by physical forces but, sometimes, weak chemical bondings also participate in adsorption process (Faust and Aly 1983). A molecule (pollutant) adhered to the solid surface is called an adsorbate, and the solid surface as an adsorbent (Fig. 8.2).

The common adsorbents include activated carbon, molecular sieves, polymeric adsorbents, and some other low-cost materials. When adsorption is concerned, thermodynamic and kinetic aspects should be involved to know more details about its performance and mechanisms. Except for adsorption capacity, kinetic performance of a given adsorbent is also of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction. Further, the solid-liquid adsorption process is influenced by parameters such as pH, solubility of solute in the solvent, solution temperature and also the initial solute concentration. Furthermore, adsorption equilibrium is the set of conditions at which the number of molecules arriving on the surface of the adsorbent equals the number of molecules that are leaving. The relation between the amount of substance adsorbed by an adsorbent and the equilibrium concentration of the substance at constant temperature is called the adsorption isotherm (Theodore and Ricci 2010). In order to determine the adsorption isotherm several models have been suggested such as the Langmuir, Freundlich, Temkin, Elovich liquid film diffusion, intraparticle diffusion and Dubinin-Radushkevich isotherm models (Table 8.2). The applicability of the isotherm equation to the adsorption study done was compared by judging the correlation coefficients (R^2) (Tan et al. 2008).

8.3.1 Adsorption Kinetics

The study of adsorption kinetics is important because it provides valuable information and insights into the reaction pathways and the mechanism of the reactions (Table 8.3). An adsorption process is normally controlled by: (i) Transport of the solute from solution to the film surrounding the adsorbent, (ii) from the film to the

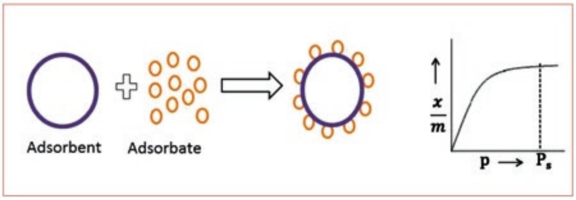

Fig. 8.2 Adsorption process

Table 8.2 Isotherm constant parameters and correlation coefficients calculated for various adsorption onto various adsorbent

Model type	Equation	Plot	Parameters
Langmuir	$\frac{1}{q_e} = \frac{1}{(K_a Q_m C_e)} + \frac{1}{Q_m}$	A plot C_e/q_e *Vs.* C_e exhibits straight line of slope $1/Q_m$ and an intercept of $1/(K_a Q_m)$	Q_m (mg g^{-1})
	$R_L = \frac{1}{1 + K_l C_0}$	If $R_L>1$ unfavourable adsorption	K_a (L mg^{-1})
		$R_L = 1$ linear adsorption	R^2
		$0<R_L<1$ favourable adsorption and $R_L=0$ irreversible adsorption	
Freundlich	$\ln q_e = \ln K_F + (1/n) \ln C_e$	A plot ln (q_e) *Vs* ln (C_e) should be straight line	1/n
			K_F (L mg^{-1})
			R^2
Temkin	$q_e = B_1 \ln K_T + \ln C_e$	Values of B_1 and K_T were calculated from the plot of q_e *Vs.* ln (C_e).	B_1
			K_T (L mg^{-1})
		K_T is Temkin adsorption potential	R^2
		B_1 Temkin constant	
Dubinin and Radushkevich (D-R)	$\ln q_e = \ln Q_s - B\varepsilon^2$	The slope of the plot of ln (q_e) versus ε^2 and the intercept yields the adsorption capacity, Q_s (mg g^{-1}). ε is Polanyi potential (kJ mol^{-1})	Q_s (mg g^{-1})
			B
			ε (kJ mol^{-1})

adsorbent surface and (iii) from the surface to the internal sites followed by binding of analyte to the active sites. The slowest steps out of all the steps determine the overall rate of the adsorption process. There are different differential equations have been used for finding kinetic model in the batch system, these equations were solved by using integral method. If the kinetic model is correct, the appropriate plot of the concentration-time data should be linear (Do 1998). These include zero order, first order, second order, third order, pseudo first order, pseudo second order, parabolic diffusion and Elovich –Type.

Table 8.3 Kinetic parameters for the adsorption onto various adsorbent

Order of the reaction	Formula	Description
Zero order	Rate = $k[A]^0$	K is the rate constant of zero order adsorption (mg $L^{-1}min^{-1}$)
	Rate = k	
	$C_t = C_i - kt$	C_i and C_t are the liquid-phase concentrations of metal ions at initial and at time t, respectively (mg L^{-1})
First order	$\ln C = \ln C_i - K_1 t$	K_1 is the rate constant of first order adsorption (min^{-1})
Second order	$\frac{1}{C_t} = \frac{1}{C_i} + K_2 t$	K_2 is the rate constant of second order adsorption (L $mg^{-1}min^{-1}$)
Third order	$\frac{1}{C_t^{\ 2}} = \frac{1}{C_i^{\ 2}} + K_3 t$	K_3 is the rate constant of third order adsorption ($mg^2.L^{-2}$ min^{-1})
Pseudo first-order kinetic	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303t}$	log ($q_e - q_t$) *Vs* t to give a linear relationship from which k_1 and q_e can be determined from the slope and intercept
Pseudo second order kinetic	$(t / qt) = \frac{1}{(k_2 q_e^{\ 2})} + \frac{t}{q_e}$	(t/q_t) *Vs* t to give a linear relationship from which k1 and q_e can be determined from the slope and intercept
Intraparticle diffusion	$q_t = K_{dif} t^{1/2} + C$	Values of K_{dif} and C were calculated from the slopes of q_t versus $t^{1/2}$
Elovich	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$	Plot the values of q_t *Vs* ln (t) to give a linear relationship from which α and β can be determined from the slope and intercept, respectively
Describing the kinetics of heterogeneous	α and β are constants of Elovich –type equation.	q_t is concentration of adsorbate in solid phase at time (t).
Chemisorption	α represents the rate of chemisorption. β is related to the extent of surface coverage and the activation energy of chemisorption	

Table 8.4 Properties of nitrate and phosphate ions

Parameter	Nitrate	Phosphate
Molecular formula	NO_3^-	PO_4^{3-}
Charge	monovalent	Trivalent
Molar mass (g mol^{-1})	62.0049	94.97
Solubility in water (Na salts) (g L^{-1})	912.0 (25 °C)	88.0(25 °C)
Ionic radius (R_{ion}) ($\times 10^{-10}$ m)	3.0	–
Hydrated radius (R_{hyd}) ($\times 10^{-10}$ m)	5.1	3.39
Hydration free energy (ΔG_{hyd}) (kJ mol^{-1})	−305.85	–
Bulk diffusion coefficient, 25 °C (D_w) ($\times 10^{-9}$ m^2 s^{-1})	1.9	–

8.3.2 Batch and Column Experiments

The adsorption capability of adsorbent toward nitrate and phosphate anions can be investigated separately using aqueous solutions of KNO_3 and KH_2PO_4. Adsorption can performed batch-wise in Erlenmeyer flasks on a temperature regulated platform stirrer under the following parameters: temperature 25–55 °C, adsorbent dosage (g L^{-1}), pH 3–8, an initial concentration mg L^{-1} analyte ions. The pH of the solutions was adjusted by adding either 0.1 M HCl or 0.1 M NaOH. The adsorbent and anion suspensions were continuously agitated with a speed of optimized speed for particular time. In case, fixed-bed column studies will be performed using a laboratory scale glass column with an internal diameter of 1 cm and a length of 12 cm. A stainless sieve was attached at the bottom of column with a layer of glass wool. A known quantity of anion solution was fed in upwards through the column. The column was operated at three different flow rates ranging 0.5–1.5 mL min^{-1} for a solution concentration of 100 mg L^{-1}, a bed height of 12 cm, pH= 3–8, and 25 °C. Effluent samples were collected at the outlet of the column at regular time intervals and analyzed for anion concentration. The breakthrough curves were obtained by plotting the ratio (C/C_o) of anion concentration (C) at time (t) to initial concentration (C_0) versus time (t).

8.3.3 Physico-Chemical Properties of Nitrate and Phosphate

The adsorption mechanism of the nitrate and phosphate ions onto adsorbents is significantly dependent on the physico-chemical properties of N and P ions and their interaction with the adsorbent surface. Properties of nitrate and phosphate such as the solubility, ionic radius, hydration energy and bulk diffusion coefficient are crucial for the selective adsorption of these ions. These are compiled from different sources (Marcus 1997; Nightingale 1959; Richards et al. 2013; Custelcean and Moyer 2007; Kumar et al. 2014). Some of the important characteristics of inorganic anions are brief in Table 8.4.

The immobilization of anions onto the adsorbent also relies on the size of the adsorbent pores, which in some cases is similar or smaller than the ionic and/or hydrated dimensions of the anions. This hindrance results in selective anionic adsorption, and further results in the formation of inner-sphere, outer-sphere complexes and electrostatic or hydrogen bonding of the anion with the adsorbent surface. However, the differences in selective anionic adsorption cannot be adequately explained by the bare ionic radii, hydrated radii, stokes radii, diffusion coefficients or charge.

8.3.4 Nanoscience and Nanotechnology

Nanomaterials have a large surface area and high chemical reactivity compared to their corresponding bulk analogues and they can be fabricated in a variety of shapes and various lattice planes are present for reactions (Taniguchi et al. 1974). This is the most important and unique aspect about the nanomaterials for their end use in environmental remediation (Pradeep 2012). Also, nanomaterials are highly dispersible and can be anchored onto solid supports for desired applications and deployed in different environments (Ali 2012). These materials either transform contaminates to the harmless products chemically or adsorb/absorb onto the surfaces/cavities and hence removing/scavenging them (Bhattacharya et al. 2013; Pradeep 2009). The main aim in this review are to highlights recent advances in the development of novel nanoscale materials for removing nitrate and phosphate ions from water system. Figure 8.1 highlights four classes of nanoscale materials that are being evaluated as functional materials for water purification: (1) zerovalent metal-containing nanoparticles (ZVMNP), (2) nanoscale metal oxide materials (3) carbon based nanomaterials and (4) functionalized nanoscale materials. These have a broad range of physicochemical properties that make them particular attractive as separation and reactive media for water purification.

8.3.5 Nitrate and Phosphate Removal Using Nanoscale Zerovalent Materials

In comparison to larger sized ZVPs, nZVPs has a greater reactivity due to a greater surface area to volume ratio (Wang and Zhang 1997). Besides, nZVNP can be potentially used directly in the field for *insitu* treatment *via* injection at almost any location and depth in soil and groundwater systems (Chekli et al. 2016). Ideally, for this type of application, ZVNPs are expected to feature several key properties including: (i) high reactivity for the removal of targeted contaminants; (ii) high mobility in porous media; (iii) high reactive longevity after injection and (iv) low toxicity to the biota in the surrounding environment. These properties are the main tool when designing ZVNPs for water treatment (Yan

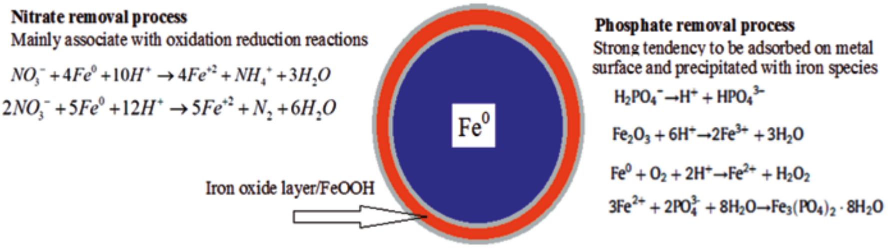

Fig. 8.3 Possible Mechanism of nitrate and phosphate removal using nZVI nanoprticles

et al. 2013). The most widely studied ZVNPs for environmental remediation is nanoscale zero-valent iron (nZVI). The synthesis of ZVI nanoparticles is relatively easy, involving the reduction of ferric ion by sodium borohydride (Wang and Zhang 1997). Typical groundwater contains many dissolved electron acceptors (nitrate or sulfate) that can react with nZVI surface and produce iron surface passivation (Fig. 8.3).

Moreover, nitrate removal is enhanced by lowering the pH by using either by adding acidic solutions or buffer system. However, addition of acidic solution like sulfuric acid (Huang et al. 1998), hydrochloric acid and acetic acid (Cheng et al. 1997) may be effective in lowering the pH but it also introduces species that has adverse impact on the quality of the drinking water. An alternative procedure to lower the pH is through the use of carbon dioxide bubbling (Ruangchainikom et al. 2006) since it can create an acidic environment by supplying the system with hydrogen ion (Hsu et al. 2004). Effect of both contaminant and solute concentrations on nZVI performance has been investigated in several studies (Table 8.5). On the other hand phosphate removal by NZVI and iron oxide nanoparticles is known to be a sorptive process, and the sorbed phosphate remains in the nanoparticles or sometimes get precipitated with iron species (Fig. 8.3).

Almeelbi and Bezbaruah 2012 have reported up to 100% removal of phosphate using nanoscale zero-valent iron (nZVI) particles and found nZVI particles to be more efficient than larger-sized particles (micro ZVI). Effectiveness of the NZVI in phosphate removal was found to 13.9 times higher than micro-ZVI (μZVI) particles with same nZVI and μZVI surface area concentrations used in batch reactors. A phosphate recovery better at higher pH and it decreased with lowering of the pH of the aqueous solution. The amount of nZVI in G-nZVI was an important factor in the removal of phosphorus by G-nZVI, and 20 % G-nZVI (20 % nZVI) would remove phosphorus most efficiently (Liu et al. 2014).

Further the specific reaction mechanism for the removal of phosphorus with nZVI or G-nZVI was mainly due to chemical reaction between nZVI and phosphorus. nZVI (Wen et al. 2014) was used to remove phosphate from aqueous solution, and the influence of pH, ionic strength and coexisting anions on phosphate removal. The results agree well with both Langmuir model and Freundlich model, and the calculated maximum adsorption capacity of phosphate was 245.65 mg/g. The removal of phosphate obviously decreased with an increasing pH due to the IEP of

Table 8.5 Performance of nZVNP for the removal of nitrate and phosphate pollutants

Adsorbent	Amount taken (mg/L)	pH and time (min)	Surface area (m^2/g)	Model and reaction rate	Adsorption capacity (mg/g)	Reference
nZVI	1–10	4 30	–	–	96–100 % PO_4^{3-}	Almeelbi and Bezbaruah (2012)
G-nZVI	1–20	– 80	–	Freundlich	14.71 PO_4^{3-}	Liu et al. (2014)
nZVI	50–90	3–5 60	39.36	first order	63–98 % NO_3^-	Alessio (2015)
nZVI	100	7 90	93.84	pseudo first-order kinetics	97 % NO_3^-	Hwang et al. (2011)
nZVI	50	11 180	17.6	Langmuir-Hinshelwood Pseudo first-order	49.8 NO_3^-	Kim et al. (2016)
nano-Fe/Cu	100	4 200	32.6	–	60 % NO_3^-	Hosseini et al. (2011)
Cu–Pd/NZVI	30	7 9 h	–	first-order		Hamid et al. (2015)
nZVI	100	6–8 5h	7.7	–	80–84 % NO_3^-	Hsu et al. (2011)
Nanoscopic Fe^0	50	3 60	39.36	first order kinetic	98 % NO_3^-	Biswas and Bose (2005)
nZVI-graphite	100	6.7 30	6.18	–	80 NO_3^-	Zang et al. (2006)
nZVI – graphene	20	– 30	–	Freundlich	15.63 NO_3^-	Peng et al. (2015)
nZVI/Fe-Ag/EDTA	1000	4 240	48.13	–	340.15 NO_3^-	Kunwar et al. (2012)

nZVI. Alessio (2015) have reported an efficiency of nitrate removal up to 98 %, 87 % and 63 % were reached in 60 min during the treatment of solutions characterized by initial nitrate nitrogen concentrations of 50 mg/L, 70 mg/L and 95 mg/L, respectively and interaction was verified found to be a first order kinetic-type. nZVI prepared by chemical reduction without a stabilizing agent and possible mechanism between nitrate ion would be absorbed on the nZVI shell structure, and then the reduction reaction occurred on the shell structure by electron transfer from the core structure (Hwang et al. 2011). Moreover, the reduced ammonium ion would be isolated to the aqueous phase, and it was stripped to the gas phase under an alkaline condition. The nitrate reduction by nZVI is a heterogeneous catalytic reaction and it governs the pseudo-first-order and pseudo-second-order adsorption kinetic equations provided a good fit for the nitrate removal whereas the Langmuir-Hinshelwood kinetic equation provided a good fit for the ammonia generation (Kim et al. 2016).

nZVI particles supported on micro-scale exfoliated graphite were prepared by using KBH_4 as reducing agent in the H_2O/ethanol system (Zhang et al. 2006). The supported ZVI materials generally have higher activity and greater flexibility for nitrate removal to the extent of 80 % in the near neutral pH range.

Bimetallic of nano-Fe/Cu particles were synthesized and used in packed sand column experiments to reduce NO_3^--N through packed sand column (Hosseine et al. 2011). The rate of reduction by bimetallic particles is significantly faster than those observed for Fe^0 alone (Wang and Chen 1999). The mechanism responsible for this reactivity is related to catalytic hydrogenation and electrochemical effect (Tratnyek et al. 2003). In addition, a higher stability for the degradation and the prevention or the reduction of the formation and accumulation of toxic by products are the advantages of bimetallic nano particles. Nitrate removal using nZVI supported Cu−Pd bimetallic catalyst (Hamid et al. 2015) in a continuous reactor system. Advantages of their study was found to be higher removal efficiency, selectivity toward nontoxic products, relatively mild conditions, and easier operation compared to other physicochemical and biological technologies.

A small pilot scale study explored the capability of nitrate removal by nZVI particles in a re-circulated flow reactor of 4.3 L liquid volume (Hsu et al. 2011). Nitrate removal of 70 % was observed with the initial pH of 6.4 with the solution being pre-purged by N gas at a rate of 50 mL min^{-1}. The solution pH needs to be controlled within the neutral range to improve the nitrate removal by the nZVI process. In another report, nitrate-contaminated water passing through reactive porous media comprising of 125 cm^3 of sand containing 0.5, 1.0, or 1.5 g of steel wool and seeded with hydrogenotrophic denitrifying microorganism was sufficient to reduce nitrate concentrations from 40 mg/L as NO_3^--N to less than 2 mg/L as NO_3^--N with a retention time of 13 days (Biswas and Bose 2005). A mathematical model was developed to evaluate the performance of nZVI materials role in nitrate reduction, ammonium accumulation and hydrogen turnover (Peng et al. 2015).The simulation results further suggest a nZVI dosing strategy (3–6 mmol L^{-1} in temperature range of 30–40 °C, 6–10 mmol L^{-1} in temperature range of 15–30 °C and 10–14 mmol L^{-1} in temperature range of 5–15 °C) during groundwater remediation to make sure a low ammonium yield and a high nitrogen removal efficiency. EDTA/Fe-Ag nanohybrid material (Kunwar et al. 2012) used for nitrate removal and this interaction verify pseudo-first-order and pseudo-second-order adsorption kinetic equations. In addition, a Langmuir-Hinshelwood kinetic equation was able to successfully describe ammonia generation, apart from nZVI dose, the ionic strength, and effect of pH.

8.3.6 Nitrate and Phosphate Removal Using Nanoscale Metal Oxide Materials

Among the adsorbents used to improve water quality standards, hydrated metal oxides like Fe(III), Zr(IV), and Cu(II) have been more extensively explored for phosphate removal (Table 8.6) because they exhibit a strong ligand sorption (of HPO_4^{2-} and $H_2PO_4^-$) through the formation of inner sphere complexes and/or

Table 8.6 Performance of nano-scale metal oxide materials for the removal of nitrate and phosphate pollutants

Adsorbent	Amount taken (mg/L)	pH and time (min)	Surface area (m^2/g)	Model and reaction rate	Adsorption capacity (mg/g)	Reference
Bayoxide-E33	140	7.0 45	120–200	Langmuir model Intra-particle diffusion studies	38.8 PO_4^{3-}	Jacob et al. (2016)
Z-La$(OH)_3$	500	2.5–10.524 hr	55.69	Langmuir model pseudo-second-order reaction	71.94 PO_4^{3-}	Xie et al. (2014)
Fe–Mg–La	100	6.4 10 h	–	Langmuir model Intra-particle diffusion studies	48.3 PO_4^{3-}	Yu and Paul Chen (2015)
Fe–Al–Mn trimetal oxide	4.7–8.7	6.8 200 min	303	Freundlich model seudo-second-order	48.3 PO_4^{3-}	Lu et al. (2013)
Fe–Ti bimetal oxide	50	6.8 32 h	39.9	Langmuir model pseudo-second-order reaction	35.4 at pH 6.8. PO_4^{3-}	Lu et al. (2015)
n-HZO	10	6.8 6 h	2.34	Langmuir pseudo first- order	21.1 PO_4^{3-}	Chen et al. (2015)
n-Mg$(OH)_2$	10	6.0–12 80–100	–	Freundlich pseudo-first-order	45.6 PO_4^{3-}	Zhang et al. (2015)
Fe_3O_4/ZrO_2/chitosan	NO_3^-(100) PO_4^{3-} (50)	3 1440	212.9	Langmuir isotherm model	NO_3^- (89) PO_4^{3-}(26.5)	Jiang et al. (2013)
MgO- biochar	–	–	–	–	NO_3^- (94) PO_4^{3-} (835)	Zhang et al. (2012)
Fe–Zrbinary oxide	0–35	5.5 6 h	339	Langmuir model pseudo-second-order	PO_4^{3-} (33.4)	Ren et al. (2012)
CuO	200	5.5 180 min	200	Langmuir model Pseudo-second-order	PO_4^{3-} (23.9)	Mahdavi and Akhzari (2016)

through outer-sphere complexes (Chen et al. 2015). Batch, equilibrium, and column experiments were conducted by using Bayoxide E33 and its derivatives to determine various adsorption parameters (Jacob et al. 2016). Equilibrium data were fitted to different adsorption isotherms and the Langmuir isotherm provided the best fit. Based on the Langmuir model, it was found that E33/Ag II has a slightly higher maximum monolayer adsorption capacity (38.8 mgg^{-1}) when compared to unmodified E33 (37.7 mgg^{-1}). The uptake of phosphate by zeolite and lanthanum hydroxide (La-ZFA) was explained on the basis of the adsorption mechanism of the ligand exchange process (Xie et al. 2014). The sorbed phosphate could be recovered by hydrothermal treatment in 3 M NaOH at 250 °C, with a simultaneous regeneration of La-ZFA. The sorbent has a high phosphate removal capacity, with a sorption maximum of 71.94 mg/g, according to the Langmuir model. The removal of phosphate by La-ZFA performs well at a wide pH range, reaching > 95 % from pH 2.5 to pH 10.5 when initial P concentration < 100 mg/L. The sorbent Fe–Mg–La with Fe:Mg:La molar ratio of 2:1:1 ($Fe(NO_3)_39H_2O$, $MgSO_4H_2O$ and $La(NO_3)_36H_2O$) was prepared through co-precipitation approach for phosphate removal in contaminated water (Yang and Chen 2015). The hydroxyl groups play a key role in the phosphate removal by the sorbent and the presence of sulfate groups also play a certain role in the uptake. The spent sorbent can be successfully regenerated by 0.5 M NaOH solution. Yu and Chen 2015 have reported three different magnetic core–shell Fe_3O_4@LDHs composites, Fe_3O_4@Zn–Al–, Fe_3O_4@Mg–Al–, and Fe_3O_4@Ni–Al–LDH were prepared *via* co-precipitation method for phosphate adsorptive removal. The surface hydroxyl groups (M–OH) may well be exchanged by the adsorbed phosphate, forming outer-sphere surface complex (M–O–P). Therefore, the removal efficiency of phosphate was more than 80 % at pH 3–7. These magnetic core–shell Fe_3O_4@LDHs adsorbents may offer a simple single step adsorption treatment option to remove phosphate from water without the requirement of pre-/post-treatment for current industrial practice.

A nanostructured Fe–Al–Mn trimetal oxide synthesized by oxidation and co-precipitation method was reported (Lu et al. 2013). The phosphate removal gradually decreased with the increasing of pH (4–10.5). The phosphate adsorption on the adsorbent was fitted by Freundlich>Temkin>Langmuir at pH 6.8. The maximum adsorption capacity for Fe–Al–Mn trimetal oxide was about 48.3 mg/g at 25 °C. Spectroscopic analyses indicated that electrostatic attraction and replacement of surface hydroxyl groups (M\OH) by phosphate via the formation of inner-sphere complex were the main adsorption mechanism. The kinetics tests indicated that the phosphate sorption on Fe–Ti bimetal oxide at pH 6.8 obeyed the pseudo-second-order kinetics (Lu et al. 2015). The Langmuir sorption capacity for phosphate was 35.4 mg/g at pH 6.8. Spectroscopic analyses indicated that phosphate sorption on the Fe–Ti bimetal oxide occurred via replacement of surface hydroxyl groups (M-OH) by phosphate. The Fe–Ti bimetal oxide effectively regenerated by NaOH solutions. Nanosized hydrous zirconium oxide (HZO) supported by a macroporous anion exchanger D-201, exhibited highly preferable removal of phosphate from water even in the presence of other commonly occurring anions at greater levels (Chen et al. 2015). The exhausted HZO-201 can be in situ regenerated by using a binary NaOH–NaCl solution for cyclic runs. A novel composite adsorbent (denoted as HMO-PN) by encapsulating active nano-$Mg(OH)_2$ onto macroporous polystyrene beads modified with fixed quaternary ammonium groups [$CH_2N^+(CH_2)_3Cl$] (Zhang et al. 2015). The N^+-tailored groups can accelerate the diffusion of target phosphate through electrostatic attractions. Kinetic equilibrium of phosphate adsorption can be achieved within 100 min, and the calculated maximum adsorption capacity is 45.6 mg/g. Moreover, the exhausted HMO-PN can be readily regenerated using an alkaline brine solution. The Fe_3O_4/ZrO_2/chitosan composite used to adsorb both nitrate and phosphate (Jiang et al. 2013). Further, this was the first report of a modified chitosan with the ability to adsorb both of these two nutrient anions. The maximum adsorption amount of nitrate and phosphate is 89.3 mg/g and 26.5 mg P/g, respectively. The adsorption process fits well to the pseudo-first-order kinetic rate model, and the mechanism involves simultaneous adsorption and intra-particle diffusion.

Zhang et al. 2012 have developed porous MgO-biochar nanocomposites by crystallizing nano-MgO flakes in biochar matrix through slow pyrolysis of $MgCl_2$-pretreated biomass. This MgO-biochar nanocomposites exhibits an excellent adsorption ability to phosphates and nitrates in aqueous solutions. The Langmuir maximum capacity of phosphate on the MgO-biochar was around 835 mg/g, which is much higher than that of other adsorbents for the removal of phosphate from aqueous solutions. The Langmuir maximum nitrate capacity of MgO-biochar sample was around 94 mg/g. Performance of Fe–Zr binary oxide towards phopshate removal was established by Ren et al. 2012. The adsorption data fitted well to the Langmuir model with the maximum P adsorption capacity estimated of 24.9 mg P/g at pH 8.5 and 33.4 mg P/g at pH 5.5. The phosphate adsorption was pH dependent, decreasing with an increase in pH value. The presence of chloride, sulphate and carbonate doesn't interfere on phosphate removal. The phosphate uptake was mainly achieved through the replacement of surface hydroxyl groups by the phosphate species and formation of inner sphere surface complexes at the water/oxide interface. A nanoscale CuO material for the removal of phosphate by adsorption method (Mahdavi and Akhzari 2016). Equilibrium adsorption data for phosphate were in good agreement with Langmuir isotherms and pseudo-second-order equation indicating its chemisorption nature adsorption capacity was found to be 23.9 mg/g of CuO

8.3.7 Nitrate and Phosphate Removal Using Functionalized and Carbon Based Material

Carbon based materials like graphite, graphite oxide (GO), graphene, carbon nanotube (CNT), multiwall carbon nanotube (MWCNT), and functionalized carbon based materials have made potential applications in adsorption and catalysis. Only a few studies are reported for the removal of phosphate and nitrate ions from aqueous system (Table 8.7). The performance of carbon residue obtained as a by-product

Table 8.7 Performance of nano-scale carbon based materials for the removal of nitrate and phosphate pollutants

Adsorbent	Amount taken (mg/L)	pH and time (min)	Surface area (m^2/g)	Model and reaction rate	Adsorption capacity (mg/g)	Reference
Carbon residue	10	4 (NO_3^-) 6 (PO_4^{3-}) 5 hr	590	Langmuir model and pseudo-second-order	30.2 NO_3^- 11.2 PO_4^{3-}	Kilpimaa et al. (2015)
CNT	200	5.6 180 min	12.1	Freundlich Isotherms Pseudo-second-order kinetic	15.4 PO_4^{3-}	Mahdavi and Akhzari (2016)
GO/ZrO_2	20	6.0 48 h	160	Langmuir adsorption isotherms	16.45 PO_4^{3-}	Zong et al. (2013)
Graphene-FeOOH-Fe_2O_3	200	6 3 h	–	Freundlich model Second order equation	350 PO_4^{3-}	Diana et al. (2015)
Graphene	100	7	–	Langmuir Second order adsorption	89.37 PO_4^{3-}	Vasudevan and Lakshmi (2012)
MCM-48 silica	300	<8 NO_3^- 4–6 PO_4^{3-} 10	750	Freundlich model	NO_3^- (71 %) PO_4^{3-} (88 %)	Saad et al. (2007)
Zr(IV)-chitosan	NO_3^- (10) PO_4^{3-} (1000)	3–10 60	9.04	Langmuir and Freundlich	NO_3^-(128) PO_4^{3-} (149)	Sowmya and Meenakshi (2014)

from wood gasification process was employed as a precursor for preparing adsorbent by physical activation (Kilpimaa et al. 2015). The kinetics showed that the adsorption data followed pseudo-second-order kinetics and Langmuir model. This may be due to the homogeneous distribution of active sites on physically activated carbon residue and commercial activated carbon. Mahdavi and Akhzari (2016) have used CNT material for the removal of phosphate by adsorption method. Further, equilibrium adsorption data for phosphate were in good agreement with Freundlich sotherm and pseudo-second-order equation indicating its chemisorption nature adsorption capacity was found to be 15.4 mg/g of CNT. ZrO_2 functionalized graphite oxide by post-grafting method and employed it as a sorbent material for the removal of phosphate ions (Zong et al. 2013). Again, the adsorption capacity of phosphate ions on ZrO_2 functionalized graphite oxide was found to be highly dependent on the pH values and decreases on increasing the pH value from 2 to 12 and attained its maximum at a pH value of 2.03. This reduction in the adsorption capacity on increasing pH was explained on the basis of variation in the extent of various types of interaction between phosphate ions and ZrO_2/graphene composite including electrostatic interaction, ion-exchange and acid base interaction. Phosphate removal based on graphene aerogel decorated with goethite (FeOOH) and magnetite (Fe_3O_4) nanoparticles (Diana et al. 2015). The aerogels showed a superior capacity to remove up to 350 mg g^{-1} at an initial phosphate concentration of 200 mg L^{-1} from aqueous system.

Graphene is an excellent phosphate adsorbent with an adsorption capacity of up to 89.37 mg/g at an initial phosphate concentration of 100 mg/L and temperature of 303 K (Vasudevan and Lakshmi 2012). The adsorption process follows second order kinetics, suggesting that the adsorption was a chemical controlling process. The adsorption of phosphate preferably fitting the Langmuir adsorption isotherm suggests monolayer coverage of adsorbed molecules. Effects of functional groups on the adsorption of $NO_3^-$and NO_2^- by carbon cloth (Afkhami et al. 2007). The carbon cloths were chemically etched in 4M H_2SO_4 solution after deionization cleaning procedure and used for the adsorption of NO_3^- and NO_2^- from water samples at nearly neutral (pH 7) solutions. Further, treatment of carbon cloth with acid produced positive sites on the carbon cloth, by protonation of surface –OH groups caused an increase in electrostatic adsorption of anions. The dramatic increase in the adsorption of anions by treatment of C-cloth with acid was attributed to the strong electrostatic interaction between the negative charge of anions and positive charge of the surface. The adsorption capacity of acid treated carbon cloth for $NO_3^-$and NO_2^- was 2.03 and 1.01 mmol/g, respectively. Powdered activated carbon (PAC) and carbon nanotubes (CNTs) were used for the removal of NO_3^- from aqueous solution (Namasivayam and Sangeetha 2005). The NO_3^- adsorption capacity of CNTs was found to be higher than PAC and decreased above pH 5. The equilibration time for maximum NO_3^- uptake was 60 min. Adsorption capacity of the PAC and CNTs was found to be 10 and 25 mmol NO_3^- per gram adsorbent, respectively.

The ordered mesoporous materials (OMM) with pore size between 2 and 50 nm were discovered in 1992 by researchers working for the Mobil Corporation. In 1998, researchers at the University of Califomia in Santa Barbara announced that they had produced silica with much larger 46–300 angstrom pores (Zhao et al. 1998) and latter the material was named Santa Barbara Amorphous type material (SBA-15). Surface modified mesoporous silica materials produced by surface functionalization *via* the tethering of organic functional groups are potential adsorbents used for removal of water pollutants. Saad et al. (2007) have reported 46 and 43 $mg g^{-1}$ adsorption capacity when using ammonium functionalized MCM-48 for phosphate and nitrate ions removal, respectively. In another report (Saad et al. 2008), synthesized and protonated several amino-functionalized mesoporous silica materials and successfully applied them to remove nitrate from water. The aminated and protonated mesoporous silica showed high adsorption capacities of 0.6–2.4 mg g^{-1} for the unmodified mesoporous silica, despite the latter having a high surface area total pore volume. Phosphate was found to reduce nitrate adsorption, therefore, special types of functionalized mesoporous silicas (SBA-15) were produced where the nitrate adsorption was less affected by phosphate due to pore size of adsorbent matching with nitrate ion. Unmodified cross-linked chitosan beads do not have the ability to remove nitrate and phosphate due to the absence of positive sites. Zr(IV) was loaded onto cross-linked chitosan beads to make the polymer selective towards the nitrate and phosphate anions (Sowmya and Meenakshi 2014). Zirconium based adsorbents have excellent anion adsorption capacities. Zr(IV) loaded sugar beet pulp was used for the removal of nitrate (Hassan et al. 2010), mesoporous ZrO_2 (Liu et al. 2008), amorphous zirconium hydroxide (Chitrakar et al. 2006) and Zr^{4+}introduced Mg-Al LDH (Chitrakar et al. 2007) were the various zirconium based materials reported for the removal of phosphate.

8.4 Conclusion

A critical evaluation of nanomaterials as adsorbents in this review article indicates that nanoparticles have been used for the removal of nitrate and phosphate species from water successfully. These nanocomposite materials are capable to remove pollutants even at low concentration, under varied conditions of pH and temperature. The dose required of nanoparticles is quite low, making their application economical. Moreover, it has been observed that the removal time is quite fast. These properties of nanoparticles made them ideal candidates for fast and inexpensive water treatment technology.

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Chapter 9
Light Driven Nanomaterials for Removal of Agricultural Toxins

Kah Hon Leong, Lan Ching Sim, Saravanan Pichiah, and Shaliza Ibrahim

Abstract Globalization has catalyzed the agricultural sector for prompting the trade across the globe with derived benefits to the growth of the nation. Many nations depend highly on the agricultural industry both for earning foreign exchange and fullfilling local needs. In the last decades the industry has emerged owing to the superior technology development and its demand in global market. As a consequence industry has contributed to the diffusion of new xenobiotics, such as pesticides, in to the aquatic environment. Pesticides are used for reducing crop infection and increasing crop yield. The usage pesticides and fungicides can rarely be stopped because of the complexity of the pests. Thus removal of xenobiotics from the aquatic environment is mandatory, since they contribute for wide range of detrimental effects to flora, fauna and well beings. Heterogeneous photocatalysis, a subset of advanced oxidation processes, is one of the means to clean waters.

Here we review the use light driven nanomaterials for remediation of agricultural pollutants. Light driven nanomaterials are very effective and convert organic pesti-

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cides into nontoxic small molecule such as carbon dioxide and water. Titanium dioxide and modified titanium dioxide photocatalysts show a good performance in eliminating the pesticides such as 2,4-dichlorophenol and 2-chlorophenol. Ag-modified titania removes 60 % of 2,4-dichlorophenol from aqueous solutions with initial concentration of 20 mg/l. The modification of the titanium dioxide increases the removal rate by 4.3 times compared to the initial titanium dioxide. Similarly, the titanium dioxide nanotubes (TNT) also exhibit an excellent performance in degrading 2-chlorophenol in the presence of visible light source.

Keywords Titanium dioxide • Advanced oxidation processes • Nanomaterials • Agricultural pollutants • Photocatalysis

9.1 Introduction

For several decades, agricultural production worldwide has increased with the use of unusual chemical fertilizers and pesticides. The rapid agricultural growth has created a series of problems related to human health and environment. Water pollution has become the global risk and continues to threaten the entire ecosystem irrespective of developed or developing nations. This is due to the complexity of agricultural pollutants discharged into the aquatic system through runoff. It becomes a challenge to identify an ideal treatment process that can eliminate them and meet environmental regulations. In addition the agricultural toxins like pesticides, insecticides and fungicides could not be treated as such that happens in any real industries. The agriculture in most Asian nations was executed in the traditional way and has millions of small scale farmers who employ all forms of toxins as pesticides etc. The continuous usage accumulated those toxins in to the surface and sub-surface aquatic systems. Several treatment methods including the *ex situ*, pump and treat and *in situ* procedures such as thermal treatment, chemical oxidation, surfactant solvent flushing, and bioremediation have been adopted to reduce the impacts from agricultural activities Karn et al. (2009). These methods are expensive and time consuming despite effective. Further, most of the agricultural pollutants contain endocrine disrupting compounds and persistent organic pollutants which are not effective taken care by any of these methods.

In the present years nanomaterials have gained a great deal of interest in the various fields including environmental. Nanomaterials are defined as materials with at least one external dimension in the size range from approximately 1–100 nm. Their reduced size and large radii of curvature make them reactive and able to scavenge the water pollutants. Nanomaterials in various morphologies or structures exert significant impact on water quality in the natural environment Diallo and Savage (2005). One dimensional nanomaterials such as nanorods, nanotubes and nanowires have been widely studied due to its ordered and strongly interconnected nanoscale architecture which could improve electron transport Yang et al. (2008). The functionalization process is applied to nanomaterials by coating method or chemical modification that improves the surface and optical properties. For example, metal or

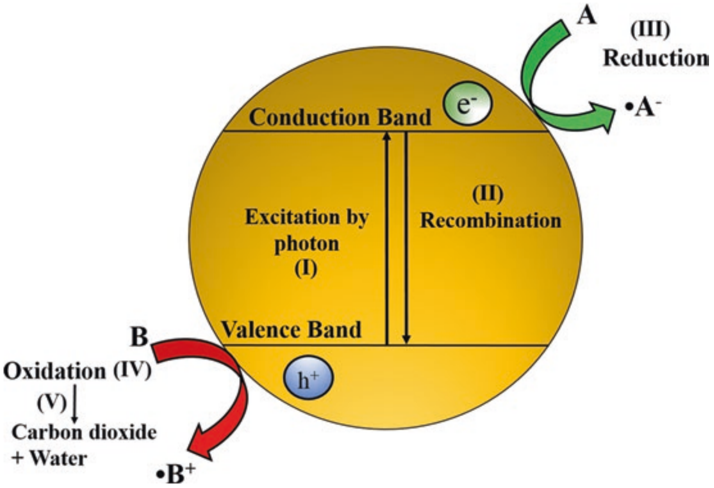

Fig. 9.1 Schematic illustration of semiconductor photocatalysis principle. The excitation takes place in presence of photons from high energy light spectrum leading to the formation of active radicals through a redox reaction. The $\bullet A^-$ and $\bullet B^+$ refers to the active radicals

non-metal doping can boost up the photocatalytic activity and reduce the band-gap of titanium dioxide, leading to absorption capability in visible spectrum and thus making them as sustainable material or photocatalyst.

9.2 Heterogeneous Photocatalysis

Heterogeneous photocatalysis a classification of Advanced Oxidation Processes plays a major role in water quality management and is recognized as one of the "foundation pillars" of green chemistry Anastas et al. (2001). In general catalyst is defined *as a substance that can accelerates a chemical reaction without being consumed as a reactant*. Meanwhile, photocatalyst is defined *as the acceleration of a reaction by the presence of a catalyst through photon energy*. Over the past decades, the application of this photocatalysis concept has proven to be promising in solving many major environmental and energy concerns like toxic organics pollutants degradation and water split reaction for hydrogen production.

The heterogeneous photocatalysis involves the presence of a semiconductor photocatalyst to initiate or accelerate specific redox reactions such reduction and oxidation. A schematic illustration of the principle of semiconductor photocatalysis is shown in Fig. 9.1. When this semiconductor photocatalyst is illuminated with photons which is equal or greater than their band gap energy, electrons and holes are generated in the valence band (Fig. 9.1(I)). Moreover, with sufficient energy driven from photons the electrons are excited from valence band to conduction band leaving behind positive holes Hoffmann et al. (1995). Thus excited electrons and formed holes migrate to the surface and perform the redox reactions.

The electrons from the conduction band possess chemical potential of +0.5 to −1.5 V versus the normal hydrogen electrode and reveal a strong reduction capacity (Fig. 9.1(III)). Meanwhile, the holes in the valence band possess chemical potential of +1.0 to +3.5 V versus the normal hydrogen electrode and exhibited a strong oxidative potential (Fig. 9.1(IV)). Thus photogenerated electrons and holes felicitate the robust redox reaction. The electron donors or electron acceptors are adsorbed on the surface of semiconductor and produces active radical, responsible for the degradation of pollutants (Fig. 9.1(V)) H. Wang et al. (2014b). During the photocatalysis, recombination of excited electrons with the holes is forced and dissipates the input energy in the form of light or heat (Fig. 9.1(II)). This recombination phenomenon occurs due to the scavenger or crystalline defects and able to trap the electrons and holes. Based on the fundamental of semiconductors photocatalyst principles, this phenomenon heavily hinders the photocatalytic efficiency.

Numerous advantages that heterogeneous photocatalysts can offer are such as (i) enrich the semiconductor light absorption ability by incorporating with metal/non-metal, other semiconductors and noble metal (ii) improving the charge separation efficiency by forming a Schottky junction (metal with semiconductor heterostructures) with build in electrical potential or p-n (semiconductor heterostructures) (iii) integration with a suitable co-catalyst can lower the redox potential Qu and Duan (2013).

9.3 Nanomaterials

9.3.1 Titanium Dioxide Photocatalyst

Over the past years, interest in the application of semiconductor photocatalyst as nanomaterials has grown tremendously attracted the environmental engineers for a full-fledged treatment of liquid and gaseous waste. These semiconductors (TiO_2, ZnO, Fe_2O_3, CdS and ZnS) embrace electronic structure of completely filled valence band and empty conduction band. The electronic structure endorses as sensitizers for light reduced redox processes Hoffmann et al. (1995). Among the many semiconductors, titanium dioxide turn out to be the most attractive and promising semiconductor as photocatalyst. This was owing to its superficies, versatile and unique characteristics that allow concurrent oxidation of water and reduction of protons. The innovative feature of titanium dioxide was first identified by Honda and Fujishima in 1972 where they discovered a photosensitization effect of titanium dioxide electrode for electrolysis of water into hydrogen and oxygen upon applying an external bias Fujishima and Honda (1972). Further it also exhibits merits including non-toxicity, chemical and biological inert, photostability, high photoactivity and economical Ding et al. (2000), Grabowska et al. (2013), Su et al. (2011), Tang et al. (2012a), Z. Wang et al. (2014a). Thus designate titanium dioxide photocatalyst as potential candidate for agricultural based pollutants.

9.3.2 *Carbon Based Nanomaterials*

Carbon nanomaterials applications in catalysis are well known and continue to grow for the past years. This type of nanomaterials is most commonly used either as support for immobilizing active species or as metal-free catalysis Machado and Serp (2012). Graphene, a recent innovation had attracted great attention due to its versatile and diversified applications. It is a flat single layer of sp^2-bonded carbon atoms firmly packed into a two-dimensional honeycomb lattice Tian et al. (2012). It possesses distinctive electronic, optical, thermal and mechanical characteristics that had great influence in photocatalysis. Their numerous unique characteristics include: large specific surface area, outstanding thermal conductivity, high hydrophobicity, great adsorption capacity, high mobility of charge carriers and high optical transmittance J. Liu et al. (2012), Machado and Serp (2012), Tang et al. (2012b), Tian et al. (2012), Xiang et al. (2012), N. Zhang et al. (2012). The oxygen functional groups in graphene oxide can be reduced to graphene with partial restoration of the sp^2 hybridization by various means including hydrothermal H. Zhang et al. (2009), thermal Schniepp et al. (2006), chemical Gao et al. (2009), electrochemical Ramesha and Sampath (2009), photothermal Abdelsayed et al. (2010), photocatalytic Williams et al. (2008), sonochemical Vinodgopal et al. (2010) and solvothermal Cao et al. (2009) methods.

Apart from the Reduced Graphene Oxide metal free polymeric semiconductor, Graphitic Carbon Nitride had very recently attracted tremendous attention of researchers for a robust and stable visible light driven photocatalyst. As compared to other inorganic semiconductor, graphitic carbon nitride consists mainly of carbon and nitrogen which are among the most abundant elements in our planet, making it a sustainable organic semiconductor. The heptazine ring structure and the high condensation degree enable this metal free semiconductor to have various notable advantages such as good physicochemical stability, harvesting visible light with a band gap of 2.7 eV, suitable redox potential to efficiently catalyze reactions, abundant, and inexpensive. These unique properties make graphitic carbon nitride a promising candidate for visible light enhancement. Nevertheless, pure graphitic carbon nitride suffers from shortcomings such as rapid recombination rate of photogenerated electron-hole pairs and a small specific surface area. However, its 2-dimensional layered structure enables it for hybridizing with other component and overcome its shortcomings.

9.3.3 *Functionalization of Nanomaterials*

The candidature of titanium dioxide has been studied extensively for decades due to their incomparable qualities. However, they have few major drawbacks on its photoexcitation domain: (i) wide band gap energy 3.2 eV (ii) higher recombination rate of photogenerated electrons and holes and (iii) low absorption ability in the visible light region. All these limitations hinder its inherent photocatalytic characteristics especially in the visible light region. Therefore, remarkable effort has been dedicated to overcome all these limitations especially in utilizing the abundant renewable energy such as solar energy, approximately 43.0 % of visible light as compare to 5.0 % of UV light. Hence, it is important to design a photocatalyst that can effectively extend the light absorption spectra to visible region in order to harvest the solar energy.

Besides that, further modification necessitates the minimization of recombination rate of electrons and holes in order to enhance the redox reaction. Tremendous modification methods through doping or composite with metal or non-metal Xiang et al. (2011), Yu et al. (2009), coupling and construction of heterojunctions H. Cheng et al. (2013), Su et al. (2012), Z. Wang et al. (2009), integration with carbonaceous material Ong et al. (2013), Sun et al. (2012) and plasmonic photocatalyst Hou et al. (2011), Lou et al. (2011), P. Wang et al. (2011), Xiao (2012) had been executed by various researchers.

9.4 Agricultural Pollutants Remediation Technologies

9.4.1 Visible Light Driven Modified Titanium Dioxide for Removing Pesticides

Recently, emphasis has been given to the combination of noble metal nanoparticles and titanium dioxide to form a unique "*Plasmonic photocatalyst*" that ascends the photocatalytic performance. Noble metals (i.e Ag, Au, Pd) in nanoparticles form acknowledge as new impurity agent for harvesting visible light energy due to their high optical absorption over a wide range of the solar spectrum Cushing et al. (2012), Linic et al. (2011). They also serve as "charge-carrier traps" to inhibit recombination of photogenerated electron-hole pairs. This strong absorption of light energy in visible region is due to its own characteristic of surface plasmon resonance effect.

The surface plasmon band is a robust and broad band in the visible spectrum of metallic nanoparticles possessing size bigger than 2 nm Shin et al. (2010). The intensity of the surface plasmon band is much dependent on the size, shape, monodispersity, dielectric constant of surrounding medium, electronic interactions between stabilizing ligands and nanoparticles Moores and Goettmann (2006). Besides, when these nanoparticles interact with titanium dioxide it promotes Schottky junction a unique feature of noble metals. This Schottky formation contributes for reduction in recombination rates of electron-hole pairs Z. Wang et al. (2012).

It is also to be noted that not all noble metal with the particles size 10 nm are capable to absorb light in the visible region as shown in Fig. 9.2. Most commonly, silver and gold nanoparticles are in favour to absorb photon energy with a relative

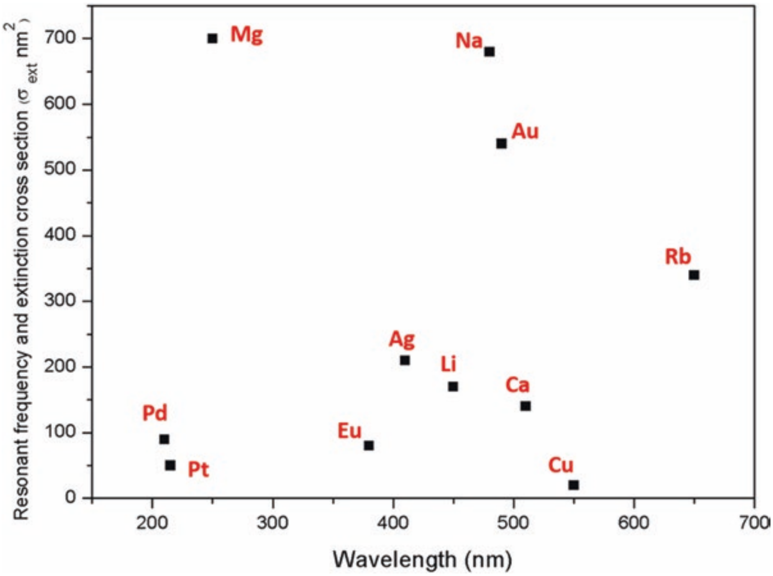

Fig. 9.2 The resonant frequency and extinction cross section for metallic nanoparticles of 10 nm. Lower the particles size in Pt and Pd results in the good absorption of high energy wavelength, where else Ag, Au etc showed strong absorption towards lower energy wavelength (Pt= platinum, Pd= palladium, Ag= silver, Au= gold)

strong excitation in the visible regime. Moreover, these two noble metals possess a characteristic of producing a stable high charge carrier density Boltasseva and Atwater (2011). However, cost of silver makes it more appropriate to be used for wider applications. Hence, many studies had been reported by other researchers on using silver as plasmonic materials Choi et al. (2010), Xiang et al. (2010), Xie et al. (2011). Where else, palladium nanoparticles with smaller size are restricted to UV spectrum. However, larger particle and clustered size overdrawn the restriction by well absorbing in the visible light regime.

The mechanism of plasmon-assisted physics is of great interest in understanding the generation and injection of excited electrons. When photon energy is absorbed, free electrons of metal nanoparticles occupy higher energy level. Considering a single electron, the excitation will take place at lower Fermi level (E_f), producing a constant distribution of primarily excited electrons at energy level between E_f and $E_f + h\upsilon$ Kale et al. (2014). This excited electron losses its energy readily right after the primary plasmon excitation through electron-electron relaxation within approximately 10 fs through non-equilibrium Fermi-Dirac electron distribution Molina et al. (2002). In this energy redistribution process, excited electron is transferred from the metal nanoparticles to the semiconductor and it fully dissipates the electron in the semiconductor Kochuveedu et al. (2013). This phenomena of equilibration of the E_f leads to bending of the semiconductor conduction band and form a Schottky barrier, prevents electron transfer from the metal to the semiconductor.

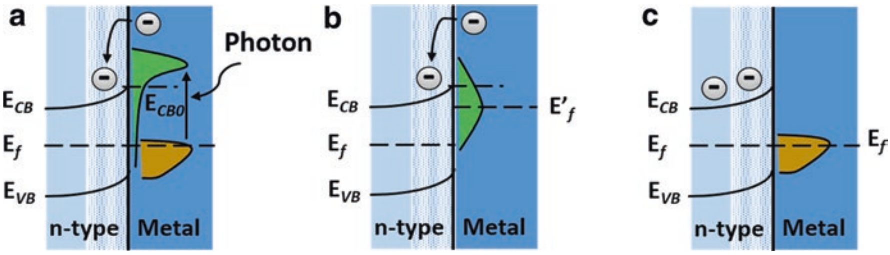

Fig. 9.3 Illustration of Surface Plasmon Resonance principle. It is evident from the illustration that the fermi level laid between the valance and conduction band. The surface plasmon contributes for the shifting of the fermi level and promotes the electron transfer between metal and semiconductor. The E_{CB}, E_{VB} , E_f and E'_f refers to energy level of conduction band, valence band, fermi level and shifted fermi level respectively

The excited electrons with energies higher than the Schottky barrier are injected into the nearby semiconductor through the surface plasmon resonance decay effect White and Catchpole (2012). The plasmonic nanostructures will then leave positively charged holes due to electron depletion. Thus generates holes undergo electron-donor process or transporting generated holes to the counter electrode in order to prevent the recombination Clavero (2014). Figure 9.3a shows the excitation of electron from the thermal equilibrium to higher energy state upon photons irradiation. While in Fig. 9.3b illustrates the collision prompted a formation of Fermi Dirac distribution at a high temperature Fermi level due to redistribution of electron energy. Figure 9.3c portraits the excited electrons flow back to the standard distribution meanwhile in the semiconductor electrons and holes flow to different regions Kochuveedu et al. (2013), X. Zhang et al. (2013).

The formation of Schottky barrier is another unique characteristic of plasmonic photocatalysts. This formation is created when a metal and a semiconductor interact with each other (Fig. 9.4). Electrons will flow from higher Fermi level to the lower in order to align the energy level at the interface of the metal and semiconductor. This equilibrium of Fermi level creates a build in electric field at the interface which will promote the charge separation of photogenerated electrons and holes by forcing the electrons and holes to move in different directions Bumajdad and Madkour (2014), Qu and Duan (2013), Jian Tian et al. (2014), H. Wang et al. (2014b).

Semiconductor titanium dioxide being a well-known photocatalyst for addressing numerous environmental concerns. It was greatly considered by the researchers over the past decades for its improvisation in order to maximize the usage of this notable semiconductor. The primary principles and mechanisms are illustrated in Fig. 9.5. When titanium dioxide is illuminated with a photon energy lesser than 390 nm, it will generate and excite an electron from the valence band to the conduction band leaving behind a positively charge hole. This excited electron where it promoted to the conduction band will then undergo oxidation with oxygen molecule to form superoxide anion radicals ($^{\bullet}O_2^-$) and followed by protonation that yields hydroperoxyl radical ($^{\bullet}HO_2$). Then, this radicals combines easily with the trapped

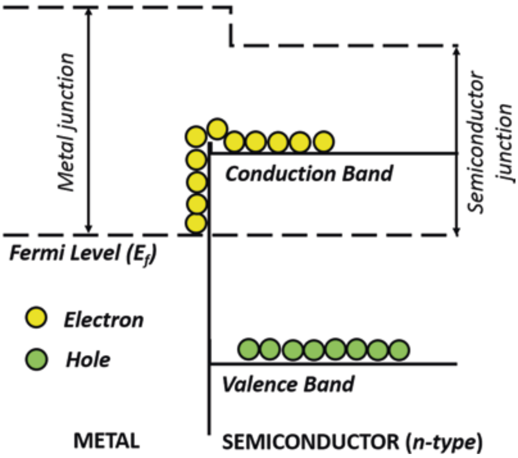

Fig. 9.4 Schematic of the Schottky barrier. This shows the Schottky barrier formation between the interface of metal and semiconductor junction and movement of electrons across the interface

electrons to form hydrogen peroxide (H_2O_2) and finally to hydroxide ($^{\bullet}OH$) an active species radicals. Meanwhile, the positively charge hole at the valence band is positive enough to generate hydroxide radicals at the surface of titanium dioxide as shown in the following equations Khataee and Kasiri (2010):

$$TiO_2 + h\upsilon\left(\lambda < 390\,nm\right) \rightarrow \mathrm{e}^- + \mathrm{h}^+ \tag{9.1}$$

$$\mathrm{e}^- + \mathrm{O}_2 \rightarrow \bullet\mathrm{O}_2{}^- \tag{9.2}$$

$$\mathrm{h}^+ + \mathrm{H_2O} \rightarrow \mathrm{H}^+ + \bullet OH \tag{9.3}$$

The hydroxide radical is an active oxidizing agent which is responsible to attack the organic pollutant present at or near the surface of titanium dioxide. It has greater potential to oxidize any form of toxic and bio resistant organic pollutant into harmless species such as carbon dioxide, water and etc. The decomposition can be elucidated through the following reactions Behnajady and Modirshahla (2006):

$$\mathrm{h}^+ + \text{Organic pollutant} \rightarrow \bullet\text{Organic pollutant}^+ \rightarrow \text{oxidation of organic pollutant} \tag{9.4}$$

$$\bullet OH + \text{Organic pollutant} \rightarrow \text{degradation of organic pollutant} \tag{9.5}$$

Modifications of titanium dioxide with different noble metals and conducting carbon materials are required to address all its limitations. Hence, it leads to photocatalytic removal of various categories of pesticides. The formation of plasmonic photocatalysts (Ag/TiO_2) had greatly shown a vast environmental remediation mainly on the removal of 2,4-dichlorophenol a common pesticides in agricultural industry. When Ag/TiO_2 is exposed to visible light irradiation, the electrons below the Fermi level (E_f) of the silver nanoparticles will be excited to the surface plasmon states, leaving positive charges below the E_f. Thus, with the contact of silver

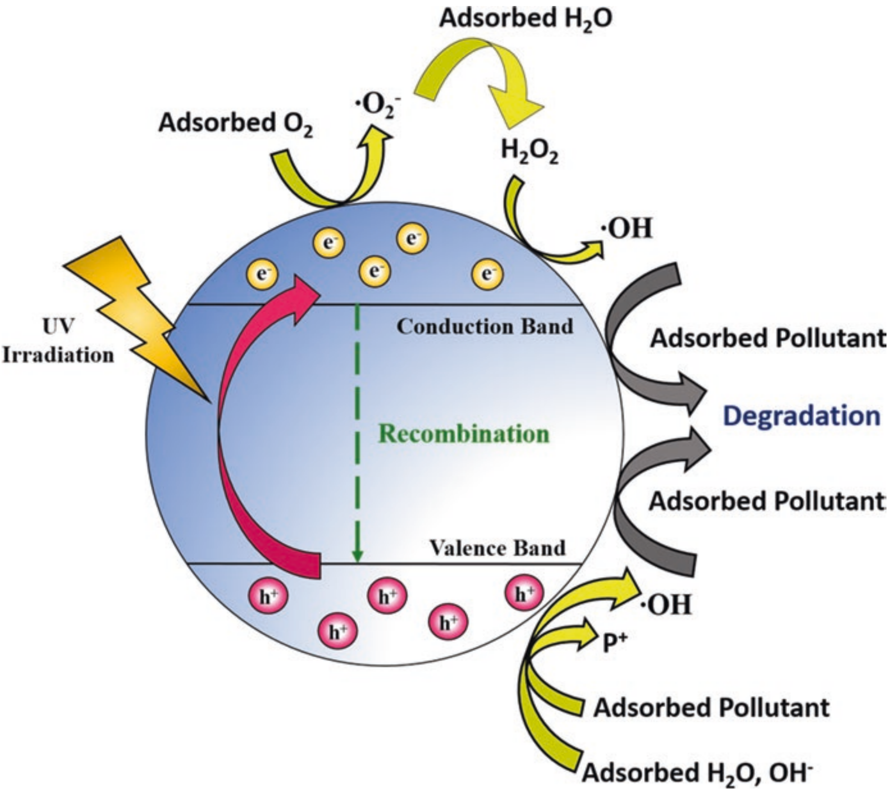

Fig. 9.5 General mechanism of photocatalysis on titanium dioxide nanomaterials. The excitation takes place in presence UV photons leading to the excitation of electrons from the valence band to the conduction band. The electrons and holes further reacts with the water for the formation of active radicals. The recombination of the electron, holes is also realistic during the photoreaction. (h^+= holes, e^-= electrons, $^{\bullet}O_2^-$= superoxide anion radical, O_2= oxygen, H_2O_2= hydrogen peroxide, $^{\bullet}OH$= hydroxide radical, OH^-= hydroxide)

nanoparticles on the surface of titanium dioxide, the energetic electrons from silver will be excited to the conduction band of titanium dioxide. As the conduction band of titanium dioxide is an electron acceptor, it is readily accepts the electrons and forms superoxide anion radicals and followed by the protonation that yields hydroperoxyl radicals. This hydroperoxyl radicals easily combines with the trapped electrons resulting hydrogen peroxide and finally forming a photodegradation active species hydroxide radicals. Moreover Schottky barrier was formed at the interface of Ag-TiO_2 because the Fermi level of titanium dioxide is higher than that of silver which will hinder the transfer of electron from the silver to titanium dioxide. However, it is proven that electrons are able to transfer from the silver to titanium dioxide due to its strong electron oscillating collectively on the surface plasmon resonance excitation. These lead to interband excitation giving sufficient energy to the electrons to overcome the Schottky barrier at the interface Kochuveedu et al.

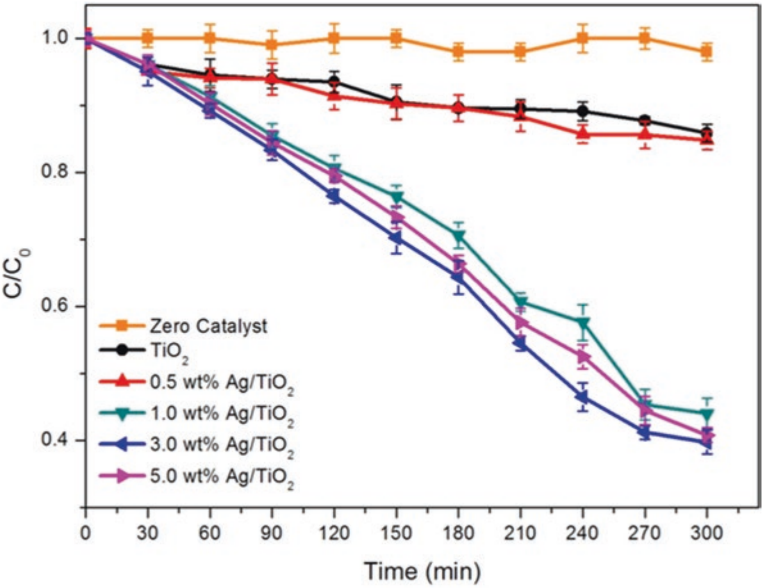

Fig. 9.6 Photocatalytic degradation rates of 2, 4-dichlorophenol under artificial visible light irradiation. The figure shows the efficacy of the modified titanium dioxide in removing the pesticide Leong et al. (2014)

(2013), Wen et al. (2011), Xiao et al. (2013). Thus it triggers the energetic electron to be transfer to the conduction band of titanium dioxide and lead to the enriched formation of hydroxide radicals thus enhancing the photocatalytic oxidation. Figure 9.6 shows the photocatalytic degradation of 2,4-dichlorophenol carry by our group under artificial visible light irradiation. The schematic propose electrons transfer is metaphorizes in Fig. 9.7.

Though the noble metals proved their candidature as a good visible light enhancer along with the suppressing the recombination rate of titanium dioxide but the achievement could not be denoted as the superior. Hence the modification of the titanium dioxide was continued by further incorporating with conducting carbon source. In addition, titanium dioxide nanotube array was proposed to overcome the post treatment separation or recovery from the slurry system after reaction. This could be defeated by titanium dioxide nanotube arrays (TNTs) which are easily recovered after treatment. Our group successfully deposited graphene oxide onto the surface of Ag-TNTs using a simple impregnation method to synthesize GO-Ag-TNTs (Sim et al. 2014). The synthesized ternary composite was used to degrade 2-chlorophenol, endocrine compound utilized in agricultural pesticides. The hydrophilic behavior of graphene oxide enabled its deposition onto the surface of silver or titanium dioxide nanotube arrays. As shown in Fig. 9.8, the prepared composite photocatalyst displayed superior photodegradation rate of 2-chlorophenol as compared to the rest.

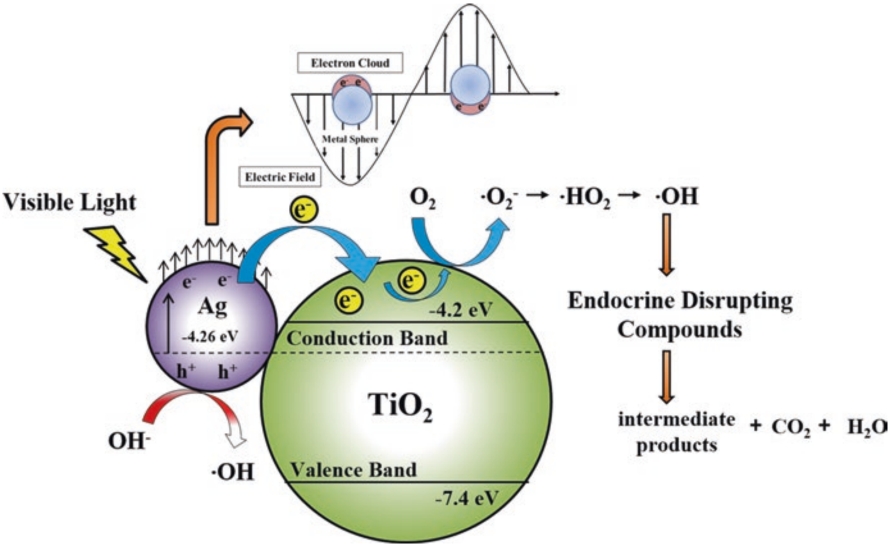

Fig. 9.7 Schematic diagram of photocatalysis mechanism Ag/TiO_2 photocatalyst under artificial visible light irradiation. The work function of the Ag excited under visible light, mobility of the electrons between the Ag and titanium dioxide is illustrated. (h^+= holes, e^- = electrons, $^\bullet O_2^-$= superoxide anion radical, O_2= oxygen, $^\bullet HO_2$= hydroperoxyl radical, $^\bullet OH$= hydroxide radical, OH^-= hydroxide, CO_2= carbon dioxide, H_2O= water)

It was well established that 4-chlorophenol and other derivatives of phenolic compounds robustly degraded under visible irradiation due to the charge transfer surface complex formation between the phenolic compound and titanium dioxide nanotube arrays Kim and Choi (2005). Such a surface complex promoted the visible light excitation through ligand-to-metal charge transfer between the 2-chlorophenol (ligand) and the Ti^{4+} site on the titanium dioxide nanotube arrays surface Wang et al. (2003), Tachikawa et al. (2004). Since 2-chlorophenol is one of the derivatives of phenolics, the surface complex formation acknowledged the 2-chlorophenol degradation as metaphorized in Fig. 9.9. Thus 2-chlorophenol compound degraded very well in the presence of pure titanium dioxide nanotube arrays compared to that of non-phenolic compound. The electrons jumped from TNTs/2-chlorophenol surface complex to conduction band of titanium dioxide nanotube arrays. These electrons were subsequently injected to silver nanoparticles and finally to graphene oxide which served as an electron sink to facilitate the separation of the excited electrons. On the other hand, the instigation of localized surface plasmon resonance in the silver nanoparticles anchored the movement of electrons to the conduction band of titanium dioxide nanotube arrays Fan et al. (2014), Chen et al. (2014).

Tang and co-worker has demonstrated that silver nanoparticles and reduced graphene oxide co-decorated titanium dioxide nanotube arrays (Ag/RGO-TNTs) exhibited almost complete (100%) photocatalytic removal efficiency of typical herbicide 2,4-dichlorophenoxyacetic acid from water under simulated solar light

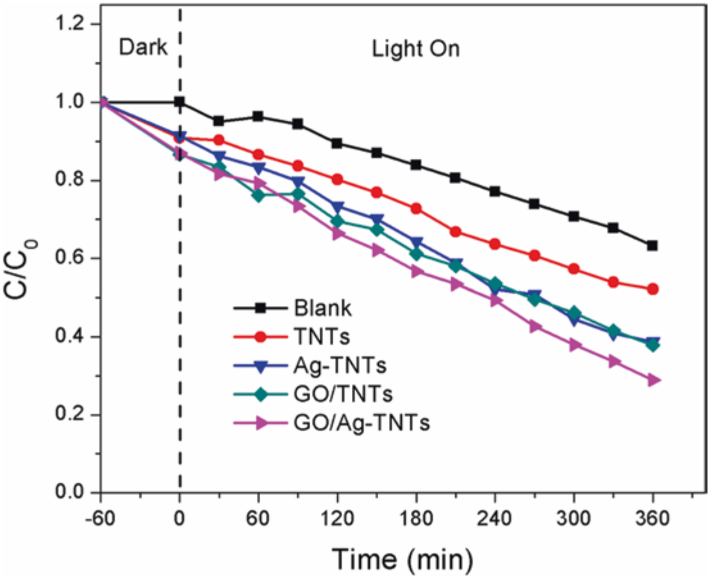

Fig. 9.8 Photocatalytic degradation rates of 2-chlorophenol for studied samples under artificial visible light illumination. The synergetic effect of the GO/Ag on to TNTs were exhibited by demonstrating 70 % removal of pesticide in the presence of visible light Sim et al. (2014) (GO= graphene oxide, TNTs= titanium dioxide nanotube arrays)

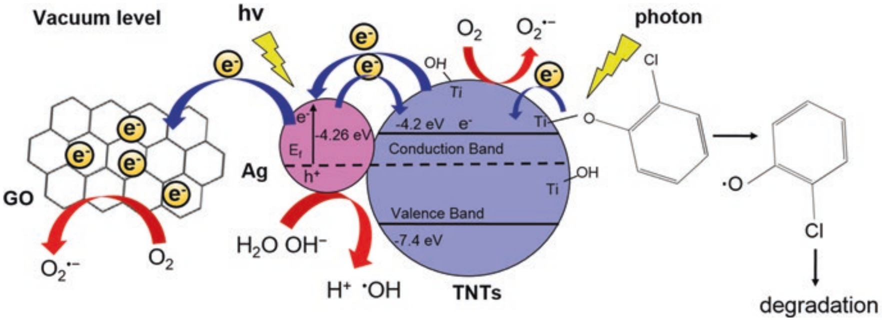

Fig. 9.9 Schematic representation of electron transfer and degradation mechanism of 2-chlorophenol. The work functions of the Ag and the movement of electron across the titanium dioxide is illustrated. The interaction of the pollutant with the composite is also depicted. (GO= graphene oxide, TNTs= titanium dioxide nanotube arrays, h^+= holes, e^-= electrons, $^{\bullet}O_2^-$= superoxide anion radical, O_2= oxygen, $^{\bullet}OH$= hydroxide radical, OH^-= hydroxide, H_2O= water)

irradiation Tang et al. (2012b). The photodegradation rate toward 2,4-dichlorophenoxyacetic acid over the composite was 11.3 times that over bare titanium dioxide nanotube arrays. After ten successive cycles, it maintained 97.3 % with excellent stability and easy recovery. As shown in Fig. 9.10, the work functions of silver (4.26 eV) and reduced graphene oxide (4.4 eV) are favourable to capture the electrons

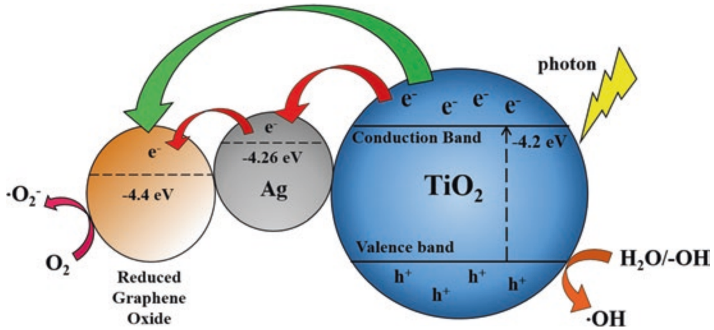

Fig. 9.10 Illustrative diagrams of electron and hole transfer in Ag/RGO-TNTs and the formation of photocatalytically active species. The work functions of the RGO, Ag and its interaction with the titanium dioxide are illustrated. (TiO_2= titanium dioxide, h^+= holes, e^-= electrons, $^{\bullet}O_2^-$= superoxide anion radical, O_2= oxygen, $^{\bullet}OH$= hydroxide radical, OH^-= hydroxide, H_2O= water)

injected from titanium dioxide. The high adsorption capacity of reduced graphene oxide increased the concentration of reactants near the surface of catalyst, promoting higher removal efficiency of 2,4-dichlorophenoxyacetic acid.

Two dimensional material graphitic carbon nitride has attracted a significant attention due to its moderate band gap, stability under thermal and photochemical condition which leads to the potential application in the remediation of agricultural pollutants. However, its low surface area, high recombination rate of photogenerated charge carriers and low quantum efficiency is limiting its practical applications. The synthesis of ultra-small gold nanoparticles supported on graphitic carbon nitride was reported for ultrafast reduction of 4-nitrophenol, a toxic agricultural pollutant generally used to prepare pesticides Bhowmik et al. (2015). The composite showed excellent catalytic activity towards the reduction of 4-nitrophenol with fast kinetics and good stability, achieving 100 % of 4-nitrophenol removal in 15s. Recently, Li and co-worker reported the reduction of 4-nitrophenol with gold nanoparticles doped mesoporous carbon nitride, 96 % conversion was happened in 300s Li et al. (2012).

9.5 Conclusion

This chapter revealed the strength of photo responsive nanomaterials for effectively removing pesticides marking a milestone in sustainable environmental remediation. Nanotechnology with the usage of the well-known titanium dioxide nanomaterials had much significant as a promising photocatalyst for agricultural remediation. However, the usage of this nanophotocatalyst material restricts its use under solar spectrum. Therefore in order to promote the sustainable and green environment, various modifications to the conventional titania had extended the light absorption region. With the activation of localized surface plasmon resonance phenomena and the formation of Schottky junction had drastically enhanced the light absorption in the visible spectrum. Meanwhile addition of carbon conducting nanomaterials significantly enriches the electron migration and prolongs the life span of the charge carrier for effective removal of these recalcitrant compounds. The titanium dioxide as nanotube's form overcome the post treatment separation i.e., recovery from slurry with promising photocatalysis characteristics. Thus, through these advanced modifications, it had the great future and potential in promoting and leads to other new pathway in environmental remediation especially in the rapid growing and most demanding agricultural industry.

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Chapter 10
Nanotechnology for Sustainable Agriculture in India

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Abstract Agriculture is essential for human survival and social sustainibility. Agriculture and society are intertwined. Agriculture is the root to solve current societal issues because ecofriendly agriculture practices can nurture ecosystems where societies rely on the services of ecosystems. Ecological imbalance, pollution, climate changes, food crises, numerous diseases, and malnourishment continue as a major concern for generations all over the world. Sustainable agriculture is the method to implement farming techniques that protect ecosystems, environment and human health, and in the same time produce adequate amount of grains, meat, plants or any life form of agriculture products for social welfare.

Here we review nanotechnology in agriculture, with special emphasis on Indian farming in Sundarbans. We summarize available nanotechnology in various fields of agriculture and food including crop productions, preservation of forest, water conservation, water resource management, waste water treatment, soil conservation, soil resource management, nutraceuticals, drug delivery, breeding of farm animals, aquaculture, fishery development, poultry farming, agrochemical, agricultural diagnostics, reestablishment of agricultural resources from natural disaster, organic agriculture, and food processing. Simplification of land ownership, correction of land maps and infrastructures development are necessary for application of nanotechnology efficiently for sustainable agriculture in India.

Keywords Sustainable agriculture • Nanotechnology • Land ownership • Land maps • Irrigation • Food processing • Water management • Agri-environment developments • Nanomachines • Sundarbans

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10.1 Introduction

In ancient era agriculture means cultivation of plants to produce food grains for survival purposes. Over the time, definition of agriculture changes, at present agriculture means cultivation of plants, trees, animals, fishes, other living materials in earth for food, medicine, clothes, shelter, environment and good quality of human life. Agriculture practices vary in each part of earth based on the quality of soil, environment and needs of local people. Earlier days agriculture practices was very simple and farmers used to produce agriculture products through natural means, that is usage of plough to prepare soils and organic matter to improve agriculture production, therefore, environment was much safe (Agoramoorthy 2015; Gross and Zhao 2014; Manyam 1995; Mishra and Sharma 2015; Misra 2001; Ranganathan et al. 2008; Sarkar et al. 2011). Due to over population, foods requirements become high on the earth resulting in usage of modern sciences and technology to increase agriculture products (Tilman et al. 2002). Usage of power tiller, tractor causes soil erosion, imbalance in ecosystems, sound pollution, imbalances of salts and minerals in soils. Excessive use of chemical fertilizers, insecticides, artificial seeds, antibiotic resistances genetically modified plants, tree and animals to increase agriculture products causes imbalance in ecosystems, diseases in human. Fishes, reptiles, birds, non-specific organisms die due to use of modern soil preparation tools, insecticides and chemical fertilizers. Death organisms not only produce environment hazards but also contribute to food crisis and extinctions of many valuable species of fishes, reptiles, and organisms (Agarwal et al. 2015).

Sustainable agriculture is the method to implement farming techniques that protect ecosystems, environment and human health, and in the same time produce adequate amount of grains, meat, plants or any life form of agriculture products for social welfare (Tilman et al. 2002; Tilman and Clark 2014). Sustainable agriculture is an idea but need to explore and develop specifically for defined agriculture practices. Sustainable agriculture may vary from agriculture to agriculture locally, nationally and internationally. Many Indian villagers depend on chemical fertilizers, insecticides for paddy cultivation to yield high produces but this may cause imbalance in ecosystems and cause human diseases; without chemical fertilizers and insecticide application in paddy field yield low produces resulting in lack of enough food to support family causes malnourishment and diseases; both ways people suffer from some sorts of difficulties. We can design experiments to explore sustainable agriculture practices efficiently in paddy field, for example co-farming of paddy and duck. Duck eats snail, insects, grass, worms, and green algae in muddy water; and during eating duck swirls water, digs soils, which is helpful for better plant growths. Duck waste can be used as manure. When paddy plants roots hold soils properly, can put duck in the rice fields. In this paddy and duck co-cultivation method we can avoid usage of chemical fertilizers, insecticides and can get better benefit from duck, duck eggs, paddy, and fishes from farmland and in addition can stabilize ecosystems. Before apply this method publicly, we need to investigate optimal paddy duck co-cultivation procedures. In addition we may explore following: (a) algae, duck and paddy co-cultivation. (b) Leguminous plants, duck followed paddy-duck cultivation. Many other combinations of agriculture practices can be explored to increase agriculture produces and improve environmental safety.

Nanotechnology is a rapidly growing field of science and technology globally and it is gaining impact on every area of science and technology. It 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. Continuous discovery of new chemical and/or physical properties of nano-scale particles provide useful functions that are being rapidly exploited in medicine, biotechnology, electronics, material science and energy sectors, among others (Parisi et al. 2015). Opportunity of nanotechnology in agriculture and food sector is prodigious and we have explored briefly option of nanotechnology in some of the sectors of agriculture. Nanotechnology promises a breakthrough in improving our conventional cultivation and food processing. It requires a thorough understanding of science, as well as fabrication and material technology, in conjunction with knowledge of the agricultural production system. The rigor of this challenge might attract brilliant minds to choose agriculture as a career (Mukhopadhyay 2014; Uskoković 2007).

Numerous discoveries have come to our civilization in science and technology (Coccia 2015; Gibbons 1999), still growing civilization continues to face ecological threats along with poverty, food crisis, energy crisis, illiteracy, natural disasters, socioeconomic hindrances (Clayton et al. 2015) because "we change and get better, things change and get better too". One of the necessary factors in the development of a healthy society is a proper socio-economic theory where sustainability of world natural resources needs eco-friendly utilization. In any age people have to come up with the questions as to how the resources of the world are to be utilized and allocated. In addition, society needs to arrange a system of government which can meet the needs of all its members. The answers which the society gives to these concerns reflect the socio-economic values that society follows. There is not only lack of mutual respect among people for utilization of world resources in an eco-friendly ways, but humans have lost all esteem, appreciation and responsibility towards the animals and plants who share this planet with us too. Our wanton destruction of the plant and animal life and our unthinking pollution of the air, earth, sea and space threaten to permanently damage the earth's eco-system making it inhospitable for all forms of life (Adhia et al. 2010; Larson 1981; Mahadevan 2013; Maheshvarananda and Branch 2010; Mishra and Sharma 2015; Phillips 2008). Therefore, sustainable agriculture is an urgent need for progressive utilization of natural resources across the globe.

In the promises of sustainable agriculture, nanotechnology can be integrated in an eco-friendly manner to offer great promise for agriculture growth, poverty reduction, food security, environmental services, public welfare, management of natural resource and securing desirable social outcomes.

10.2 Households Agriculture in Sundarbans in the State of West Bengal, India

India is 3rd largest in Asia and the 7th largest country with second highest population in the world. Color coded areas show distribution of land in India (http://www.indiawaterportal.org/articles/land-use-map-india-national-institute-hydrology): Arable land-yellow, green-forest, brown-non-agricultural, violet-scrub and grass, brownish yellow-unused land (Fig. 10.1). India has enormous amount of natural resources still number of poor and malnourished people is much higher. Around 70 % people live in village and 30% in urban areas. Agriculture is the main economy and sources of earning for many villagers. India has developed in many aspects in agriculture both in research and farming still there are huge scope for improvement and modernization of agriculture practices. Soil surface, soil quality and weather vary tremendously throughout the India. Irregular surface and height of land made

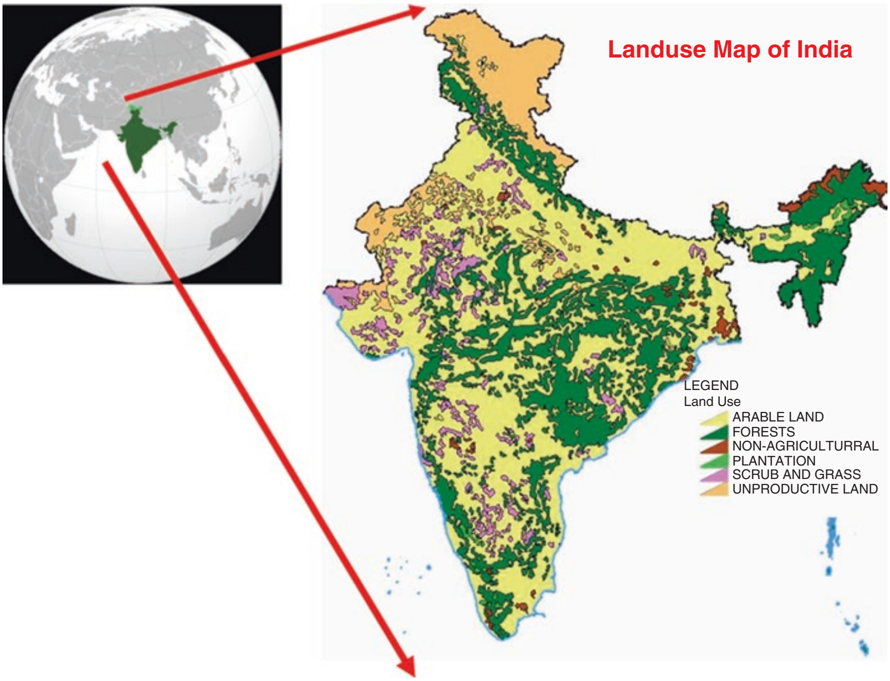

Fig. 10.1 Map of India describing distribution of usable lands for agricultures (http://www.indiawaterportal.org/articles/land-use-map-india-national-institute-hydrology; https://en.wikipedia.org/wiki/India#/media/File:India_(orthographic_projection).svg)). The map describes distribution of lands such as arable land, forests, non-agricultural, plantation, scrub and grass lands, and unproductive land. According to India Water Portal report based on the information from the national institute of hydrology in the year 2009, in India, about 51.09 % of the land is under cultivation, 21.81 % under forest and 3.92 % under pasture. About 5.17 % of the total land is uncultivated waste, which can be converted into agricultural land. The other types of land comprises up 4.67 %

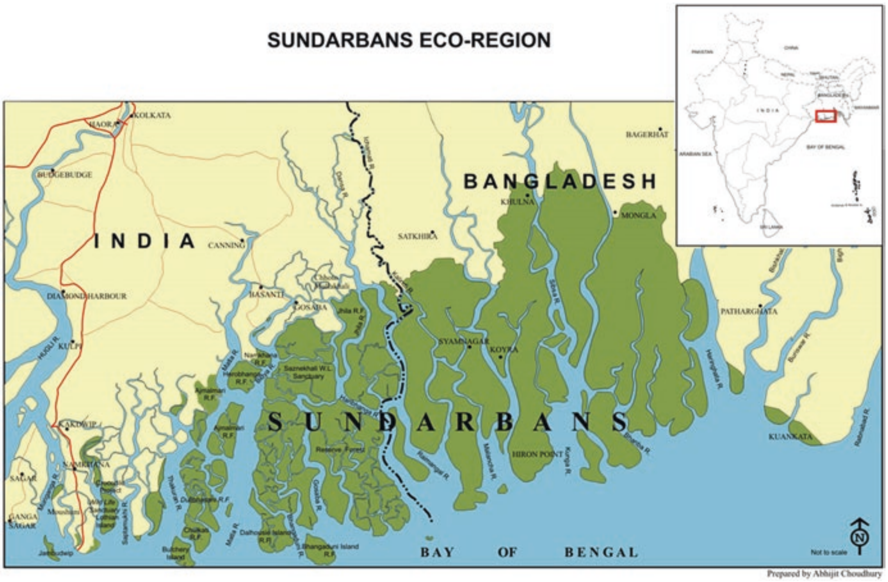

Fig. 10.2 Land map of Sundarbans describing small deltas, rivers and surrounding sea Bay of Bengal (http://assets.wwfindia.org/img/original/sundarban_map.jpg). The Sundarbans is a natural region comprising southern Bangladesh and a part in Eastern India. The Sundarbans mangrove forest, one of the largest forests in the world, lies on the delta of the Ganges, Brahmaputra and Meghna rivers on the Bay of Bengal. It is considered as World Heritage site. The site is intersected by a complex network of tidal waterways, mudflats and small islands of salt-tolerant mangrove forests, and presents an excellent example of ongoing ecological processes. The area is known for its wide range of flora and fauna, including *Sundari* trees, different bird species, the Bengal tiger and other threatened species such as the estuarine crocodile and the Indian python (Mandal et al. 2013)

it difficult to install universal irrigation systems all over India. Flood and natural calamities cause big difficulties in agriculture. Any single method of agriculture practice will not work throughout the country. For sustainable agriculture we need to devise specific methods in every part of India. We are inhabitant of Sundarbans and have seen the land status and agriculture situation for a long period of time in regular basis.

Here, we like to critically review and put our personal observation about agriculture status in Sundarbans which is a World Heritage Site in the state of West Bengal, India so that we can perform research, share knowledge and support to invent new methodologies and technologies for sustainable agriculture using available technology including nanotechnology.

Sundarbans are group of islands situated in part in West Bengal, India and other part in Bangladesh (http://assets.wwfindia.org/img/original/sundarban_map.jpg). The river Ganges, Matla, Malancha, Haringhata, and other small rivers pass through delta islands in Sundarbans and connected to Bay of Bengal. Some parts of islands are connected with arable water sources and other parts with saline water (Fig. 10.2). Inhabitants in Sundarbans rely on agriculture especially paddy cultivation, fisheries, animal husbandry, catching fishes from deep sea, collect honey from forests. Because islands are connected with rivers and sea, frequently agriculture field are spoiled with flood from saline sea water, heavy rains resulting in damage of agriculture.

Lands in Sundarbans are surrounded by muddy boundaries. Agriculture lands are segmented into small areas to keep rain water for paddy cultivation. There are no proper irrigation and drainage systems in most part of agriculture lands; therefore, heavy rain or rising water in sea causes river boundary damage and saline water enter into agriculture lands causing massive damage in agriculture in most part of Sundarbans, subsequently villagers suffer badly. In summer villagers use water from ponds for irrigation but many cases water supply is not sufficient for paddy agriculture or any other kind of agricultures. Irrigation systems are not properly installed. Land owners make boundary around lands to keep water. During heavy rain farmers need to cut land boundary to remove excess waters. Water cannot be immediately removed because of any connected irrigation and drainage systems as a result paddy, chilli, potato, water melon and other vegetables plants emerges in water for week or more causing huge damage in agricultures. There are highways pass through part of Sundarbans. The canals both sides of highway are the main water drainage systems in many villages but many parts of canals are blocked due to soil deposition or building houses, shops causing massive problem in drainage systems especially in rainy reasons resulting in irreversible damages of crops in every years. Sundarbans are made of mostly with clay type of soils that is easy to erosion causing more problems in drainage and irrigation systems. There are no easy way to solve these problems, but need to explore several possibilities and possibly install concrete-made irrigation and drainage systems to improve the situation.

Most of the pavements in villages are muddy, inconvenient for transportation of saplings, ploughing machines, ripen paddy. In many cases farmers carry saplings, paddy and other heavy equipment for farming process which is not efficient enough, incurring loss in farming products in lands before reach to farmer house.

Farmers produce agriculture products, use or sell it in local market and excess of it preserve for short or long term storage, due to lack of storage facility farmers cannot store farming products in good conditions for long period of time. Green vegetables are spoiled; and paddy, dried chili and other farming products are infected by microbes and insects during storage resulting in consumption of infected unhealthy food causing diseases.

In addition to conventional agriculture, Sundarbans have potential to develop small industry for fisheries, animal husbandry, forestry, honey bees cultivation and honey processing. We need to establish systematic approaches to build these sectors. Local peoples grow cow, goat, hen and other animals in domestic ways, veterinary services is not easily accessible for urgent uses causing massive death of domestic animals seasonally especially hens which may spread diseases to environment. Because of unorganized animal husbandry, farmers cannot collect animal stools correctly or do not collect at all. Animal's stools have potential to use as fertilizer in sustainable agriculture to avoid use of chemical fertilizers.

We can practice sustainable agricultures, nanotechnology for seeds, organic fertilizers but need to establish basic infrastructure for efficient use of technology and resources in agriculture. Farming is mostly not profitable in India causing many farming activities technologically unviable. We need central approaches to overcome the shortcoming causing by individual unorganized farming practices. Aim of the discussion on Sundarbans is to assess current status of Sundarbans and to develop it as model agriculture fields to implement modern science and technology including nanotechnology more efficiently in sustainable agriculture practices. In summary, we wish this information will help scientists, policy makers and common people to build infrastructure and implement nanotechnology in sustainable agriculture practices.

10.3 Agriculture and Society

Agriculture and society are interconnected with each other. Agriculture appears as an origin to solve current societal issues because agriculture practices can nurture ecosystems where society reliance on ecosystem services (Tilman et al. 2002). Farmers are the principal architect of global useable lands and will shape, perhaps irreversibly, the surface of the Earth in the coming decades. Farmers are the chief coach of terrestrial useable lands, which we broadly define as all land that is not desert, tundra, rock or boreal (Daily et al. 2000; Lichtfouse et al. 2009; Tilman et al. 2002). Basic integrated relation of agriculture with society was shown in Fig. 10.3. Wild agricultural forests can minimize flooding by slowing snowmelt and water discharge, moderate regional climate, and remove and store atmospheric carbon dioxide, a greenhouse gas. Forest and grassland ecosystems can create or regenerate

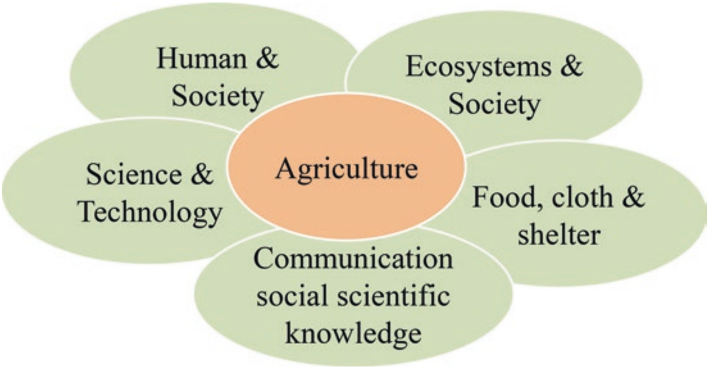

Fig. 10.3 Basic integrated relation of agriculture with society has been shown. Agriculture is the chief of society. Development of any healthy society needs a healthy ecosystems, food, cloth, shelter, ecofriendly human activity, socio-economic, socio-scientific and -technological knowledge. Agriculture plays momentous role in the every aspect of an active healthy society

fertile soils, degrade plant litter and animal wastes, and purify water, and this regenerative process is essential for subsistence slash-and-burn farming systems. The recharge of streams and aquifers by intact ecosystems provides potable water for little more expense than the cost of its extraction (Tilman et al. 2002). Thus, agriculture plays a significant role for the development of a healthy society.

10.4 Sustainable Global Agriculture

Artificializations are increasing dramatically during the global industrial, modern scientific, technological revolutions. The advent of modern artificial modern science and technology systems allowed in the saving time of farming, labor cost, manpower and rapid transportation of goods over long distances. Social groups and nations began to be less and less independent and began to rely on other countries for food and goods. This worldwide behavior led to tremendous benefits on global society that has significantly increased the human lifetime. On the contrary, this also leads to worldwide negative consequences such as World Wars I and II. Besides, artificializations also affect global agriculture through global climatic changes, changes in monsoons, decrease of gross domestic product (GDP), increase of global average temperatures due to greenhouse gas emissions, occupational health risk, and pollution in air, water and soil (Lichtfouse et al. 2009). However, human-driven ecosystem simplification and species losses accelerate worldwide, a growing body of experimental and theoretical literature has emerged to examine the effects of biodiversity losses on ecosystem functioning. Our society needs to place the value of multiple attributes of ecosystems ranging from agricultural productivity and crop impregnation to the maintenance of viable species populations. Therefore, a critical review need to examine the effects of species losses on multiple ecosystem functions simultaneously where sustainable agriculture can build bridge a prosperous society with healthy ecosystem (Gamfeldt et al. 2008; Zavaleta et al. 2010).

The objective of sustainable agriculture is to provide best services to society from agricultural production of food, fiber and from ecosystem services. This will require increased crop produces, increased efficiency of nitrogen, phosphorus and water use, soil nutrient, pollution free air, ecologically based management practices, judicious use of pesticides and antibiotics, and major changes in some livestock production practices. Advances in the fundamental understanding of agroecology, biogeochemistry and biotechnology that are linked directly to breeding programs can contribute greatly to sustainability (Cassman 1999). A basic relationship of sustainable agriculture in term of biodiversity with ecosystem was shown in Fig. 10.4.

Core development of nanotechnology are diffusing in the technological convergence across the fields of physics, engineering, chemistry, biology, agriculture, and food sciences (Kumari and Yadav 2014; Sekhon 2014). However, when nanotechnologies in agriculture and food are considered, public attitudes and the regulatory awareness are quite different. In the consequence of the debate on genetically modified organisms in agriculture and food, nanotechnology applications and

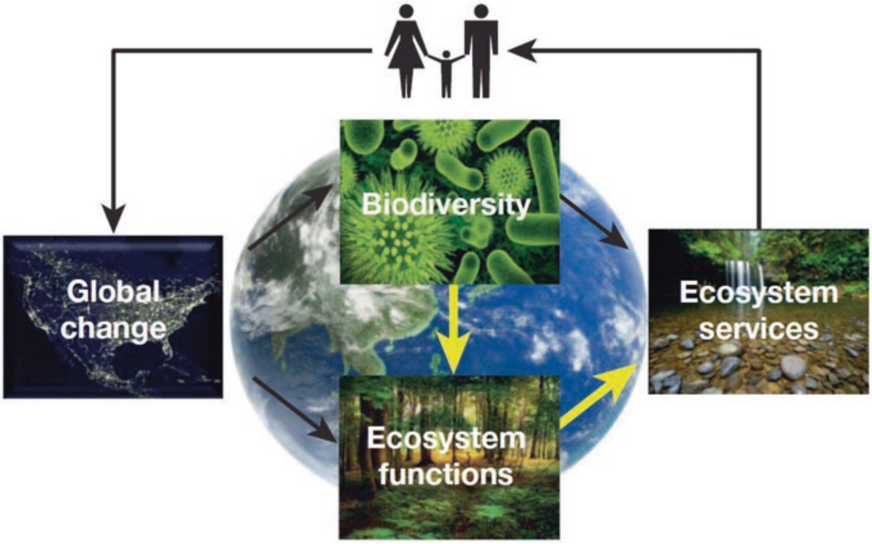

Fig. 10.4 Relation of ecosystem with humanity. Biodiversity loss and its impact on humanity has been shown (Cardinale et al. 2012). Biodiversity is the most extraordinary feature for the functions and services of the ecosystem. Biodiversity deprivation can affect functions and services of the ecosystem. Ecosystem services are depending on biodiversity and function ecosystem. Ecosystem services are the suite of welfare that ecosystems provide to humanity. Unfortunately, real scenario of world reflects that human actions are dismantling the ecosystems, eliminating genes, species and biological traits at an alarming rate which lead to severe global changes and issues. One of the necessary factors in the development of a healthy society needs a proper ecofriendly socio-economic theory for sustainable utilization of the world resources order to bring about the welfare of all members who share the world with human

nanomaterials are often critically reviewed, even by the regulators. Despite of many years of scientific and regulatory debate on benefits and risks, it remains difficult to gain an overview about the current state of research and development of nanotechnology in agriculture and food (Grobe and Rissanen 2012). Thus, implication of nanotechnology in an ecofriendly manner with agriculture may be beneficial for the sustainable growth of agriculture. Moreover, the main necessary factor in the development of a healthy society needs a proper ecofriendly socio-economic theory for sustainable utilization of the world resources order to bring about the welfare of all members who share the world with human.

10.5 Global Food Crises: Nano-agri Integration

The number of undernourished people in the world remains tremendously high (Wright et al. 2012). Food crises continue as a pestilence concern for generations all over the world. Although many efforts have been devoted to overcome food crises, challenges such as growing competitions for natural resources, emerging climate changes, natural disasters, poverty, illiteracy, industrial revolution, political turmoil/chaos, environmental collapses and diseases are posing a continuous threats to agriculture which is the main source of food security (Wu et al. 2014). The Food and Agriculture Organization of the United Nations predicts that annual meat production of 200 million tons will be required by 2050 to respond to the food needs brought about by increasing global population (Sekhon 2014). A recent joint report of the state of global food insecurity, the WHO, World Food Program, and International Fund for Agricultural Development estimate that nearly 870 million people (12.5 % of the global population and 14.9 % of those living in developing countries) are undernourished, defined as consuming insufficient energy (McGuire 2013; Moffitt and Cajas-Cano 2014). Continuous efforts of scientists to improve agricultural and food security seek joint efforts from different technologies to alleviate appropriate strategies for defeating food crises and malnutrition. With rising food crises, sustainable agricultural development plays a central role to overcome global food crisis. The rates of global population growth surpass the rate of yield growth for crop feedstock; the world faces a food crisis that requires unprecedented intellectual, financial, societal, technological, and material investments. It is observed that household farmers in mixed cropping and livestock systems produce about half the world's food (Wright et al. 2012).

Food crises directly links and negatively affects human and environmental health, the global dietary transition is one of the great challenges facing humanity. Meaningful solutions will not be easily achieved. Solutions will require analyses of the quantitative linkages between agriculture with the ecological and human health, on which it needs environment friendly efforts from agriculture, biotechnology, nanotechnology, health science, veterinary science and animal husbandry, food technology along with other scientific, sociological and technical efforts (von Braun 2010). It also requires the full deployment of every plant breeding technology currently available, including the generation of crops via transgenesis (Laible et al. 2015). But even more importantly, it necessitates a reemphasis on innovation, greater diversification of the household agricultural policy and need joint efforts in the large scale development in sustainable agriculture, nano-biotechnology and agri-biochemical industry along with other industrial supports (de Oliveira et al. 2014; Tilman and Clark 2014). Attempts to apply diverse technology in agriculture began with the growing realization that rational cultivation policy would neither be able to sufficient increase gross productivity any further nor restore ecosystems damaged by existing technologies back to their pristine state. Long-term effects of farming in conjunction with fertilizers, hybridization, pesticides and agrochemicals have been questioned both at the scientific and policy levels, and must be gradually phased out (Mukhopadhyay 2014).

Nanotechnology is a field that applies nanoscale principles and techniques to understand and transform living or nonliving systems and uses this principle on the biological and non-biological area to create new devices and systems integrated from the nanoscale. The basic processes of life at the molecular subcellular mechanisms, formation of the tissue's primary structures, molecular organelles of cell constructions are occur at the nanoscale (Roco 2003). The critical feature of nanotechnology is not only the size at which manufacture occurs (~1–100 nanometers), but also the ability to control and manipulate the biological, chemical, physical, and mechanical properties that emerge at this scale, including increased conductivity, optical properties, and reactivity (Paradise et al. 2009). For this reason, understanding the design of biological systems can shape the development of life sciences and medicine, as well as of highly efficient and versatile new devices and systems. Since the physical and chemical infrastructure of non-biological systems also constructed at subatomic particles; the understanding the design architecture subatomic particles is a main challenge in the interdisciplinary where sustainable agriculture looks to form bridge among the nanotechnology technicians, agriculturist, engineers, medics and scientists (Roco 2003).

10.6 Crop Productions with Nanoparticles

Over the last few decades, arrays of exploratory enquiry continue to ascertain the potential impact of nanotechnology on crop production improvement. A few comprehensive reports have presented on evaluation of a varieties of nanomaterial, mostly metal-based and carbon-based, for their absorption, translocation, accumulation, and importantly, effects on growth and development in an array of crop plants (Nair et al. 2010; Rico et al. 2011; Sonkaria et al. 2012). In the landmark of "good and bad" some of these studies have exposed negative effects of nanomaterial on plant growth, whereas as others report positive results. The positive morphological effects included enhanced germination percentage and rate; length of root and shoot, and their ratio; and vegetative biomass of seedlings in many crop plants including corn, wheat, ryegrass, alfalfa, soybean, rape, tomato, radish, lettuce, spinach, onion, pumpkin and cucumber. Recent research on nanoparticles in a number of crops has evidenced for enhanced germination and seedling growth, physiological activities including photosynthetic activity and nitrogen metabolism, mRNA expression and protein level, and also positive changes in gene expression indicating their potential use in crop improvement (Kole et al. 2013). Thus, uptake, translocation, and accumulation of nanoparticles into plants are crucial point for plant growth.

10.7 Preservation of Forest as Natural Agricultural Resources

The forest products industry relies on a vast renewable resource base to manufacture a wide array of products that are indispensable to our modern society. Universal preservation for the development of a healthy society in general corroborates the economies of agriculture and forestry. Nurturing natural biodiversity and producing renewable materials such as food, wood, water, and energy are often presented as being contrary to each other. However, this does not entirely manifest as contradiction because nature directly provides resources which are essential to farmers, forest producers and daily life of society. The universal-ecosystem services provided by nature and especially by biodiversity include the provision of food and non-food as well as protective functions related to air, water, carbon cycle, and climate. However, progressive utilization of natural resources and their proper utilization for welfare of all in this entire universe relies on forests live which are home of plants, animals and other family member of our ecosystem. Maintaining and enhancing self-regulating mechanisms such as nutrient cycling, soil rehabilitation and decomposition of organic matter, groundwater recharge or pollination reduces the requirements of artificial input for taking care of agriculture and forest. Many wild plants and animals depend on the existence of agricultural land use and the proximity to forests. Even though the production of generally one single crop dominates on the field itself, the border-structured neighboring cultivatable land remains an area of high biodiversity. Many species live in border landscapes between forest and agricultural used land including small streams, fens or swamps. Moreover, a number of wild animals are beneficial for agriculture such as pollinators, which depend on agri-ecosystems for survival.

Nanotechnologies may offer potential to develop entirely new approaches for producing engineered wood, fiber-based materials, nanofluidics and nanomechanics, nanochemicals and nanobiomaterials. They can also enable the development of a wide range of new or enhanced wood-based materials and products that offer cost-effective substitutes for non-renewable materials used in the manufacture of metallic, plastic, or ceramic products. Nanotechnology could transform the forest products industry in virtually all aspects-ranging from production of raw materials, to new applications for composite and paper products, to new generations of functional nanoscale biomass. Sustainable research and development in nanotechnology is critically important to the economical and sustainable production of these new generations of forest-based materials that will meet societal needs while improving forest health and contributing to the further expansion of the biomass-based economy. Nanotechnology can define how woody plants self-assemble and developing methods that use self-assembly is critical to developing novel nanoscale-based biomaterials. With respect to molecular cell biology of plants for wood industry, nanotechnology focus area seek to understand and exploit the architecture and processes of consolidation of wood cell walls which are the primary determinants of the material properties of wood and wood fibers. Wood cell walls are composites of cellulose, hemicelluloses, protein, and lignin. They form the basis of the forest products industry and its renewable resources. Wood cells contain unique protein complexes that use activated glucose to assemble cellulose nano-fibrils, the most abundant renewable material resource on earth. These remarkable cellulose nano-fibrils exhibit a modulus roughly one quarter to one fifth of that of a carbon nanotube, yet they are produced naturally without the need for energy-consuming, high-temperature processing.

Combination of biotechnology and nanotechnology can be used to tap the enormous undeveloped potential that trees possess as photochemical factories that produce rich sources of renewable raw materials using sunlight, water, and carbon dioxide. The consumption of carbon dioxide in the production of these raw materials provides a carbon sink for this important greenhouse gas. Moreover, bio-nanotechnology can provide benefits that extend well beyond fiber production and new materials development and into the areas of sustainable energy production, storage, and utilization. For example, bio-nanotechnology may provide new approaches for obtaining and utilizing energy from sunlight based on the operation of the plant cell. Thus, finding novel new ways to produce green energy, chemicals, and other innovative products and processes from the renewable resources will help to address major issues related to growth and development facing across the society (Liu et al. 2015).

10.8 Water Conservation, Water Resource Management and Waste Water Treatment

Securing and managing access to clean water is a challenge both for developing and for more economically developed countries. Water management technologies include filtration using membranes, chemical treatment, heat and ultraviolet treatment and distillation. They seek to remove solid and other contaminants or to neutralize them. Several water treatment systems have been used for producing water for domestic, industrial and agriculture. Water resource management is a momentous element in the conservation of water and in optimizing its use. A sustainable water management seeks the methods for identifying the amount of contamination in water and determining its suitability for use, as well as those for ascertaining how much water is needed and source of contaminations (Iavicoli et al. 2014). It is gaining newer significance particularly for three key purposes: (i) treatment and remediation, (ii) sensing and detection, and (iii) pollution prevention (Dasgupta et al. 2015; Powell et al. 2008). A basic application of nanotechnology for water resource management has been shown in Fig. 10.5 (Qu et al. 2013b).

Nanotechnology-based water treatment technologies being developed and used to improve desalination of sea and saline water, safe reuse of wastewater, disinfection and decontamination of water, i.e., biosorption and nanoadsorption for contaminant removal, nanophotocatalysis for chemical degradation of contaminants, nanosensors for contaminant detection, different membrane technologies including reverse osmosis, nanofiltration and photocatalysis (Bora and Dutta 2014; Kumar et al. 2014). Water purification using nanotechnology exploits nanoscopic materials such as carbon nanotubes and alumina fibers for nanofiltration. Nanofiltration is a relatively recent membrane filtration process used mostly to remove solids, including bacteria and parasites, in surface and fresh groundwater. The solar-powered system uses nanofiltration membranes to treat the local saline water, resulting in

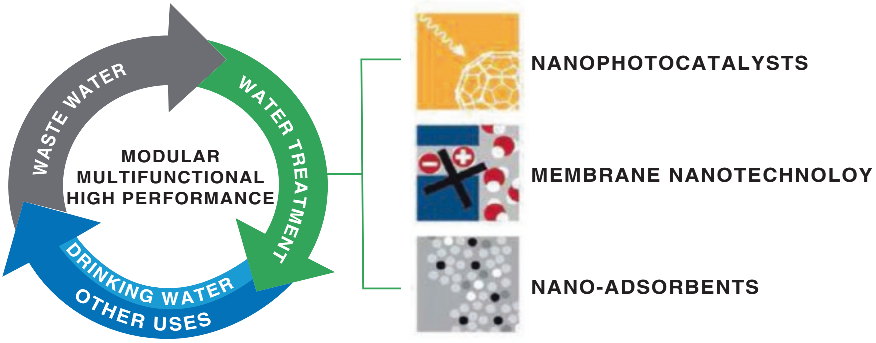

Fig. 10.5 A basic flow chart of nanotechnology for water resource management has been shown (Qu et al. 2013b). Nanotechnology approaches can be used for the improvement of photocatalysis process, membrane technology, and adsorption process

high-quality desalinated irrigation water. Crops grown with desalinated water required 25% less irrigation and fertilizer than saline water irrigation (Kumar et al. 2014; Sekhon 2014). Monodisperse magnetite nanocrystals can be used for arsenic purification as it has strong and irreversible interaction with arsenic. Additionally, magnetic properties of this nanocrystals remain intact (Yavuz et al. 2006). Sodium chloride salt from water can be effectively filter using nanoporous grapheme. The water permeability of sodium chloride salt is several times higher in nanoporous grapheme than conventional reverse osmosis membranes (Cohen-Tanugi and Grossman 2012; O'Hern et al. 2015; Zhu et al. 2013).

Tropical countries like India, agriculture heavily depends on seasonal natural water resources. Unfortunately, seasonal water also some time irregular due global climate change along with other environmental problems which become threats on agriculture. To manage fast growing demand of water, it needs multidimensional technological support along with nanotechnology in water and wastewater treatment. A short summary nanotechnology application in water and wastewater treatment has been shown in Table 10.1.

Although laboratory studies shows potential impact of nanotechnology water/wastewater treatment processes, still their commercial application for community service under development. Some methods use chemicals, are energetically costly, can be difficult to implement and manage, require substantial investments in term of funds, human capital and infrastructures, are not sufficiently adapted to local expertise and situations and may depend on having large infrastructures. Issues such as cost effectiveness, potential nanomaterial toxicity, and social acceptability must be addressed. Most nanotechnology based treatment options are high-performance; enabling more efficient treatment; but their costs are currently high. A conceptual improvement to water treatment through nanotechnology has been shown in Fig. 10.6.

Table 10.1 Some applications of nanotechnology in water and wastewater treatment have been shown here (Qu et al. 2013a). Application included in the development of adsorption processes, membranes and membrane processes, photocatalysis, disinfection and microbial control, and sensing and monitoring of low concentration of certain contaminants in the wastewater. Most applications described below are still in the stage of laboratory research

Applications	Representative nanomaterials	Desirable nanomaterial properties	Enabled technologies
Adsorption	Carbon nanotubes	High specific surface area, highly assessable adsorption sites, diverse contaminated carbon nanotubes interactions, tunable surface chemistry, easy reuse	Contaminant preconcentration or detection, adsorption of recalcitrant contaminants
	Nanoscale metal oxide	High specific surface area, short intraparticle diffusion distance, more adsorption sites, compressible without significant surface area reduction, easy reuse, some are superparamagnetic	Adsorptive media filters, slurry reactors
	Nanofibers with core-shell structure	Tailored shell surface chemistry for selective adsorption, reactive core for degradation, short internal diffusion distance	Reactive nano-adsorbents
Membranes and membrane processes	Nano-zeolites	Molecular sieve, hydrophilicity	High permeability thin film nanocomposite membranes
	Nano-Ag	Strong and wide-spectrum antimicrobial activity, low toxicity to humans	Anti-biofouling membranes
	Carbon nanotubes	Antimicrobial activity (unaligned carbon nanotubes)	Anti-biofouling membranes
		Small diameter, atomic smoothness of inner surface, tunable opening chemistry, high mechanical and chemical stability	Aligned carbon nanotube membranes
	Aquaporin	High permeability and selectivity	Aquaporin membranes
	Nano-TiO_2	Photocatalytic activity, hydrophilicity, high chemical stability	Reactive membranes, high performance thin film nanocomposite membranes
	Nano-magnetite	Tunable surface chemistry, superparamagnetic	Forward osmosis

(continued)

Table 10.1 (continued)

Applications	Representative nanomaterials	Desirable nanomaterial properties	Enabled technologies
Photocatalysis	Nano-TiO_2	Photocatalytic activity in UV and possibly visible light range, low human toxicity, high stability, low cost	Photocatalytic reactors, solar disinfection systems
	Fullerene derivatives	Photocatalytic activity in solar spectrum, high selectivity	Photocatalytic reactors, solar disinfection systems
Disinfection and microbial control	Nano-Ag	Strong and wide-spectrum antimicrobial activity, low toxicity to humans, ease of use	Point-of-use (POU) water disinfection, anti-biofouling surface
	Carbon nanotubes	Antimicrobial activity, fiber shape, conductivity	POU water disinfection, anti-biofouling surface
	Nano-TiO_2	Photocatalytic reactive oxygen species (ROS) generation, high chemical stability, low human toxicity and cost	POU to full scale disinfection and decontamination
Sensing and monitoring	Quantum dots	Broad absorption spectrum, narrow, bright and stable emission which scales with the particle size and chemical component	Optical detection
	Noble metal nanoparticles	Enhanced localized surface plasmon resonances, high conductivity	Optical and electrochemical detection
	Dye-doped silica nanoparticles	High sensitivity and stability, rich silica chemistry for easy conjugation	Optical detection
	Carbon nanotubes	Large surface area, high mechanical strength and chemical stability, excellent electronic properties	Electrochemical detection, sample preconcentration
	Magnetic nanoparticles	Tunable surface chemistry, superparamagnetism	Sample preconcentration and purification

10.9 Soil Conservation and Soil Resource Management

Soil health is the foundation of productive farming practices. Fertile soil provides essential nutrients to plants. Important physical characteristics of soil-like structures and aggregation allow water and air to infiltrate, roots to explore, and biota to thrive. Diverse and active biological communities help soil resist physical degradation and cycle nutrients at rates to meet plant needs. Soil health and soil quality are terms used interchangeably to describe soils that are not only fertile but also possess adequate physical and biological properties to “sustain productivity, maintain environmental

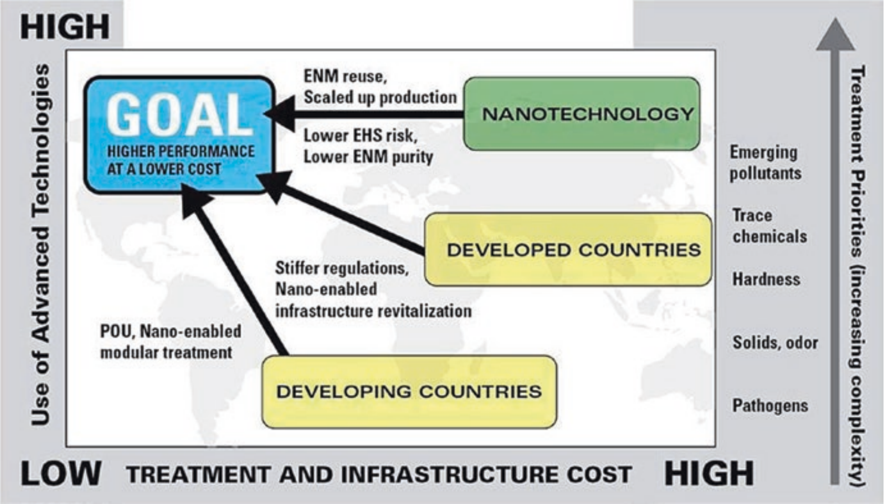

Fig. 10.6 Conceptual improvements to water treatment through nanotechnology approach. *Arrows* represent specific strategies or drivers that can enhance performance and/or decrease costs through use of nanotechnology (Qu et al. 2013b). Object/goal of nanotechnology approach is to achieve a high performance in water treatment with a low cost. Most nanotechnology based treatment options are high-performance; enabling more efficient treatment; but their costs are currently high. Environmental pollution risks are also high concern. These represent a significant drawback but not an insurmountable barrier. ENM indicates engineered nanomaterials. EHS indicates environmental health and safety. POU indicates point-of-use devices in water treatment process

(Amundson et al. 2015). Soil-crop system is one of the most important pathways of human exposure to hazardous elements. Soil-crop system may suffer different contamination inputs such as, traffic, industry, atmospheric deposition, mining leaching, waste disposal, urban activities, pesticides, and fertilizers. Soil conservation is the prevention of soil from erosion or reduced fertility caused by overuse, acidification, salinization or other chemical soil contamination (Medina et al. 2015).

10.10 Nutraceuticals, Drug Delivery and Breeding of Farm Animals

Improving the feeding efficiency and nutrition of agricultural animals, minimizing losses from animal diseases, and turning animal by-products and waste and environmental concerns into value-added products are among applications of nanotechnology in animal husbandry (Chen and Yada 2011; Sekhon 2014). Reproductive performance of livestock animals influences the productivity of agriculture worldwide (Kuzma 2010). Artificial insemination technology has great potential to improve efficiency of livestock reproduction of many non-human animals, including sheep, horses, cattle, pigs, dogs, pedigree animals generally, zoo animals, turkeys and even honeybees. It may be used for many reasons, including to allow a male to inseminate a much larger number of females, to allow use of genetic material from males separated by distance or time, to overcome physical breeding difficulties, to control the paternity of offspring, to synchronize births, to avoid injury incurred during natural mating, and to avoid the need to keep a male at all such as for small numbers of females or in species whose fertile males may be difficult to manage (Sekhon 2014). Both sire-fertility testing and semen purification can potentially be improved through the application of nanotechnology. The identification of biomarkers (e.g. ligands of lectins from *Arachis hypogaea* and *Lens culinaris*, sperm proteins ubiquitin and post-acrosomal, WW domain-binding protein) and trials of nanoparticle-based technologies for fertility testing and the nanopurification of bull semen for commercial artificial insemination have been reported. Meat can also be cultured to produce laboratory-grown meat in the form of in-vitro meat without killing the animals using nanotechnology. In huge demand of nutritional quantity and quality to fill the stomachs of hungry people in the coming years, nanotechnology may be an alternative approache (Sekhon 2014).

10.11 Aquaculture and Fishery Development

Aquaculture and fishery have been globally recognized as the fastest growing food production sector which plays a major role in meeting the increasing demand for protein requirement. In the growing essence of aquaculture, it is needed to supply future aquatic food needs. Aquaculture faces several problems such as disease outbreaks, chemical pollution, the environmental destruction and inefficient feed utilization. Therefore, sustainability of present aquaculture is now becoming questionable. Over the decades several strategies projected from national and international level, as improved laboratory facilities, diagnostic expertise, and control and therapeutic strategies in order to handle disease outbreaks more effectively.

Aquaculture and fishery industries are quite lack behind and sufficient progress has not met in order to develop aquaculture sector. In the consequence of controlling disease prevalence and ensure better health of system and sustainable production, aquaculture and fishery demand seek technological innovation for the drug use, disease treatment, water quality management, production of tailored fish for suiting better health, productivity drive by epigenetic and nutrigenomic interaction, better breeding success by efficient delivery of maturation and spawning inducing agent, nutraceutical delivery for rapid growth promotion and culture time reduction, successful use of auto-transgenic and effective vaccine. Nanotechnology with the biotechnology has projected an innovative potential to revolutionize agriculture and allied fields including aquaculture and fisheries. For these multiple purposes effort, importance of nanotechnology and nanodelivery of drugs, vaccine, nutraceutical, inducing hormones, hybridization and growth promoting anabolic open tremendous opportunity (Aklakur et al. 2015).

10.12 Poultry Farming

Use of nanoparticles can produce poultry products at a much faster pace with high safety. Antibiotic application is common in poultry farming, where the use of antibiotics in animal nutrition caused development of antibiotic resistant pathogen microorganisms. Recently, in many countries, and especially in Europe, antibiotic based growth promoters have been prohibited. Nevertheless, intensification of animal production and reduced immunity of highly productive animals require search for new growth promoting alternatives to antibiotics. A noble metal such as silver and its ions has long been known to have unique anti-bacterial properties, but even small doses of ionic silver may be toxic, limiting the use of silver as anti-bacterial agent in animal production.

Nanotechnological methods allow for producing nanoparticles of silver (nanobiotic-Ag), which may exhibit unique biological properties. It can be expected that by using nanobiotic-Ag, toxicity could be minimized or eliminated and the risk of developing resistance and transmission of resistant microorganisms to humans through food products can be highly reduced. Antimicrobial properties of nanobiotic-Ag has been observed when used in poultry nutrition, may affect microbial population without inducing microbial resistance. Furthermore, nanobiotic-Ag may increase anabolic activities, leading to stimulation of development and growth of animals (Sekhon 2014). Silver nanoparticles with hydroxyproline (Ag-Hyp) complex significantly up regulate expression of the FGF-2 at the mRNA and protein levels. Moreover, Ag-Hyp significantly increased blood vessel size, cartilage collagen fibre lattice size and bundle thickness of chicken embryos. AgHyp treatment may help to build a stronger and longer lasting form of collagen fibers chicken embryos (Beck et al. 2015).

Platinum nanoparticles (NP-Pt) are noble metal nanoparticles with unique physiochemical properties that have recently elicited much interest in medical research. However, still little is known about their toxicity and influence on general health. Effects of NP-Pt on the growth and development of the chicken embryo model with emphasis on brain tissue micro- and ultrastructure have been reported. These preliminary results indicate that properties of NP-Pt might be utilized in brain cancer therapy, but potential toxic side effects must be elucidated in extensive follow-up research (Prasek et al. 2013). Thus, the social outcome of the nanoparticle is valuable in term of animal health maintenance.

10.13 Plant Genetics, Disease, Diagnosis and Prevention

Nanotechnology has potential to protect plants, monitor plant growth, detect plant diseases, and plant breeding. Genetically encoded nanosensors have been developed on several metabolites to provide a basic set of tools for the determination of cytosolic and subcellular metabolite levels in real time by using fluorescence microscopy (Deuschle et al. 2005). Nanodevices can target specific sites to deliver nutrients and pesticides; nanocarriers can be used controlled chemical release system for plant. Nanocapsules would help to avoid phytotoxicity on the crop by using systemic herbicides against parasitic weeds. Nanoencapsulation can also improve herbicide application, providing better penetration through cuticles and tissues, and allowing slow and constant release of the active substances. Nanoparticles have a great potential as 'magic bullets', loaded with herbicides, chemicals or nucleic acids, and targeting specific plant tissues or areas to release their charge. Viral capsids can be altered by mutagenesis to achieve different configurations and deliver specific nucleic acids, enzymes or antimicrobial peptides acting against the parasites (Perez-de-Luque and Rubiales 2009). Importantly, it was experimented that DNA and chemicals can be delivered into plant cells and intact leaves through surface-functionalized silica nanoparticles (Torney et al. 2007). It was observed that a honeycomb mesoporous silica nanoparticle system with 3 nm pores that can transport DNA and chemicals into isolated plant cells and intact leaves. Using this technique, genetic modification can also be achieved to trigger defense responses of activated by pathogens. Likewise, advancement of molecular and cellular biology tools by using nanotechnology are also expected to provide disease prevention and treatment in plants e.g. disease diagnosis, screening and treatment, in farming practices involving, vector and pest detection and control (Sharma et al. 2012). Some of the nano particles that have entered into the arena of controlling plant diseases are nano forms of carbon, silver, silica and alumino-silicates (Sharma et al. 2012).

10.14 Agrochemical, Fertilizers and Pesticides

Nanoagrochemicals, nanofertilizers, nanopesticides or nano plant protection products represent an emerging technological development in relation to agrochemicals, fertilizers, pesticide use that could offer a range of benefits including increased efficacy, durability, and a reduction in the amounts of active ingredients that need to be used. Nanomaterials come in many diverse forms (surprisingly often $\gg$100 nm), from solid doped particles to (often non-persistent) polymer and oil-water based structures (Gogos et al. 2012). A number of formulation types have been suggested including emulsions (e.g., nanoemulsions), nanocapsules (e.g., with polymers), and products containing pristine engineered nanoparticles, such as metals, metal oxides, and nanoclays. Nanopesticides cover a wide variety of products, some of which are already on the market. They cannot be considered as a single entity; rather such nanoformulations combine several surfactants, polymers (organic), and metal nanoparticles (inorganic) in the nanometer size range (Kookana et al. 2014).

Nanomaterials serve equally as additives (mostly for controlled release) and active constituents (Gogos et al. 2012). A controlled-release formulations of imidacloprid (1-(6 chloro-3-pyridinyl methyl)-N-nitro imidazolidin-2-ylideneamine), synthesized from polyethylene glycol and various aliphatic diacids using encapsulation techniques, have been applied pest management in different crops (Adak et al. 2012b). The bioefficacy of the prepared controlled-release formulations was evaluated against major pests of soybean, namely stem fly, *Melanagromyza sojae* Zehntmer and white fly, *Bemisia tabaci* Gennadius along with a commercial formulation. Most of the controlled-release formulations of imidacloprid gave significantly better control of the pests compare to its commercial formulations, however the controlled-release formulations, Poly [poly (oxyethylene-1000)-oxy suberoyl] amphiphilic polymer based formulation performed better over others for controlling of both stem fly incidence and Yellow Mosaic Virus infestation transmitted by white fly. Some of the developed controlled-release formulations recorded higher yield over commercial formulation and control. Nodulation pattern of soybean was not affected due to treatment of controlled-release and commercial formulations of imidacloprid. Also the residues of imidacloprid in seed and soil at harvest were not detectable for both controlled-release and commercial formulations (Adak et al. 2012a). Controlled-release formulations of carbofuran and imidaclopridwere prepared employing polyvinyl chloride and carboxymethyl cellulose and their bioefficacy was evaluated against the aphid, *Aphis gossypii* and leafhopper, *Amrasca biguttula biguttula* Ishida on potato crop. The controlled-release formulations of carbofuran and imidacloprid provided better or equal control of the pests than commercial formulations. Carboxymethyl cellulose based formulation provided a superior control of both the pests (Kumar et al. 2011).

A nanofertilizer refers to a product that delivers nutrients to crops in one of three ways. The nutrient can be encapsulated inside nanomaterials such as nanotubes or nanoporous materials, coated with a thin protective polymer film, or delivered as particles or emulsions of nanoscale dimensions (DeRosa et al. 2010). Nanofertilizers intended to improve the nutrient use efficiencies by exploiting unique properties of nanoparticles. The nanofertilizers are synthesized by fortifying nutrients singly or in combinations onto the adsorbents with nano-dimension. Both physical (top-down) and chemical (bottom-up) approaches are used to produce nanomaterials, and the targeted nutrients are loaded as it is for cationic nutrients (NH_4^+, K^+, Ca^{2+}, Mg^{2+}) and after surface modification for anionic nutrients (NO_3^-, PO_4^{2-}, SO_4^{2-}). Nano-fertilizers are known to release nutrients slowly and steadily for more than 30 days which may assist in improving the nutrient use efficiency without any associated ill-effects (Subramanian et al. 2015). Carbon nanotubes were recently shown to penetrate tomato seeds (Khodakovskaya et al. 2009), and zinc oxide nanoparticles were shown to enter the root tissue of ryegrass (Lin and Xing 2008). This suggests that new nutrient delivery systems that exploit the nanoscale porous domains on plant surfaces can be developed. Ideally, nanotechnology could provide devices and mechanisms to synchronize the release of nitrogen (from fertilizers) with its uptake by crops; the nanofertilizers should release the nutrients on-demand while preventing them from prematurely converting into chemical/gaseous forms that cannot be absorbed by plants. This can be achieved by preventing nutrients from interacting with soil, water and microorganisms, and releasing nutrients only when they can be directly internalized by the plant (DeRosa et al. 2010).

10.15 Agricultural Diagnostics and Drug Delivery with Nanotubes

Many plant secondary metabolites serve a defensive or protective function (ecologically) for the plants against attack by insects (de Oliveira et al. 2014). Seasonal agriculture in nature depends on many variables such as soil, crops, weather, etc. Sensing, acquisition, manipulation, storage, and transfer of reliable and accurate data about the plant and production handling environment is, therefore, crucial in managing this variability to optimize both inputs and outputs and reduce impacts on the environment to meet the demand for high and good quality products. Based on advances in nanotechnology research, a new scanning probe-based data storage concept called 'millipede' was developed that combines ultrahigh density, terabit capacity, small form factor, and high data rate. Other developments include nanosensors to monitor the health of crops and magnetic nanoparticles to remove soil contaminants. Dispersed throughout fields, a network of nanosensors would relay detailed data about crops and soils. The sensors will be able to monitor plant conditions, such as the presence of plant viruses or the level of soil nutrient. Nanofabricated devices offer the scope for their injection into plants to detect tissue parts affected by rare phenomena such as diseases, nutrient deficiency, and developmental abnormalities (de Oliveira et al. 2014; Yashveer et al. 2014). Importantly, nanomaterial based formulations are also beneficial in sustainable agriculture. The benefits of nanomaterial based formulations: (i) improve the efficacy due to higher surface area; (ii) increase the systemic activity due to smaller particle size and higher mobility and (iii) decrease the toxicity due to elimination of organic solvents in relation to conventionally used pesticides and their formulations (de Oliveira et al. 2014; Sekhon 2014). Considering the development of nanotechnological carrier systems for botanical insecticides such as azadirachtin (Indian neem), limonene (citrus), nicotine (common tobacco), and menthol (peppermint) has been applied in agriculture instead of chemical pesticides (Fig. 10.7). The main biocides that have been

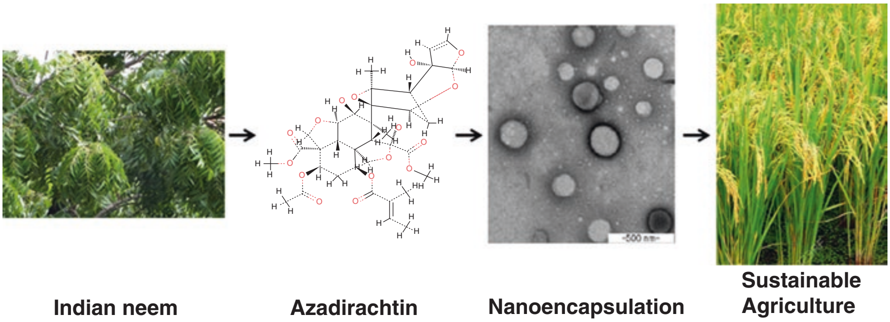

Fig 10.7 Schematic representation of the nanoencapsulation of botanical insecticides for sustainable agriculture (de Oliveira et al. 2014). Nanomaterial based formulations are important resources having beneficial effects in sustainable agriculture. Development of nanotechnological carrier systems for botanical insecticide azadirachtin has been applied in sustainable agriculture instead of chemical pesticides

used are described, together with the advantages that these systems offer over conventional approaches, and their future potential (de Oliveira et al. 2014).

10.16 Reestablishment of Agricultural Resources from Natural Disaster

Disasters disrupt and destroy shelter, life and infrastructure facilities (roads, river, airports, electricity, medical facilities, academics, food, etc.); however most affected situations are observed on agriculture systems such as water, land and instrumental facilities. We have had natural disasters (droughts, flash floods, cyclones, avalanches) created by the 1999 Odisha cyclone, India, 2004 Indian Ocean earthquake and tsunami along with the tsunamis in Asia and Japan, the earthquakes in Nepal, India, Haiti and China, as well as hurricane Katrina and others in North and Central America. The recent flooding in many parts of across the globe (e.g. 2014-2015, floods in India) caused by heavy monsoon rain which has caused unprecedented devastation and great loss of life which have been etched in our minds due to their magnitude.

In 2009, the Aila cyclone reached the east part of India and the Bangladesh. It was a devastating storm like this has not hit the Sunderbans within the last three decades (Bhalla 2009; Bhattacharyya et al. 2010; Roy 2009). The Sunderbans area was heavily affected by this tropical storm. The strong wind was blown at more than 120 km/h and has therefore destroyed the area (Fig. 10.8). It uprooted a huge number of trees, removed the roof of thousands of houses and even completely ruined them. Furthermore, the water level of the river was raised and the river embankments were not resisted to the storm. The 13 blocks of the South 24-Parganas were heavily affected and were underwater for long period of time. The saline water was covered the fields and the pond areas with a depth of more than 5 feet. Due to the heavy flood, the roads were damaged or totally destroyed. Saline water contains high concentration of sodium chloride (NaCl), potassium (K^+), magnesium (Mg^{++}) and calcium (Ca++), sulphate (SO^{4--}) ions (Gale 2006) which are detrimental for growth of agricultural plants such rice, potato, chlli and other vegetables. Saline water covered agriculture lands in Aila affected area can be improved by gypsum but implementation of nanotechnology may help to reclaim land fastest way. Nanofiltration technique is a relatively advanced membrane filtration process which might be useful to remove salts, minerals, bacteria and parasites in saline water to recover flood affected areas.

On the other hand, some other countries e.g. Japan, Thailand that have experienced natural disasters have relied on the use of technology to help minimize the hardship endured. The recent flooding in Thailand in 2011 has proved that nanotechnology can play a role in natural disaster mitigation (nano tech 2012, Tokyo; http://asia.iop.org/cws/article/news/48902). The use of nanotechnology as one of natural disaster mitigation tools has received positive feedback from end-users which helps to reinforce the need for Thailand to continue it nanotechnology

Fig. 10.8 Cyclone Aila affected Sunderbans in the year 2009. Different areas of Sunderbans were tremendously damaged due to cyclone, Aila. Houses were flooded and collapsed due to heavy rain and over flowing of the saline water. The roads were damaged or totally destroyed. The breakage of the riverbank was one of the main causes of the flood. Agriculture lands were logged with saline water caused farming destructions for years, decades (Bhalla 2009; Bhattacharyya et al. 2010; Roy 2009)

development program which is geared towards social and economic development. Some areas of nanotechnology for the mitigation of natural disasters (nano tech 2012, Tokyo): (i) water-filtration technology for cleaning water in areas contaminated with heavy metals and fertilizers; (ii) long-life insecticide-impregnated mosquito nets and mosquito-repellent lotions; (iii) smart fertilizers that respond to the life cycle of plants such as rice, sugarcane and orchids; (iv) nano-marking as safety tags for products containing nanoparticles; (v) smart soil consisting of carbonaceous soil or biochar from water hyacinth or biomass to condition soil (Sandhu 2007, 2008, 2009). Nanomachines offer distinct advantages over conventional nanoremediation agents. Such tiny machines add a new dimension based on motion to decontamination processes, lead to new *in situ* and *ex situ* nanoremediation protocols, and have the potential to reduce the cleanup time and overall cleanup costs. In particular, the continuous movement of such nanoscale objects can be used for transporting reactive (water-purification) nanomaterials throughout contaminated samples, for releasing remediation agents over long distances, and for imparting significant mixing during detoxification processes. Eventually, one would expect autonomous multifunctional “remisense” nanomachines, coupling the remediation and sensing of pollutants into the same platform, analogous to theranostic particles used for biomedical applications. Thus, nanoremediation capabilities may open up the door for efficient cost-effective routes for environmental remediation (Gao and Wang 2014).

10.17 Nanomachines in Agri-food Development

Sustainable agriculture and food processing need continuous mechanical machines for farming, soil processing, water irrigation etc. The definition of nano-agri-food processing is that nanotechnology techniques or tools are used during cultivation, production, processing, or packaging of the agricultural and food processing. It does not mean atomically modified agricultural/food produced by nanomachines (Dasgupta et al. 2015; Ranjan et al. 2014).

Agricultural work includes a great deal of heavy work and special work postures, imposing a large physical strain on farmers (Davies 2009). Usage of heavy machines such as power tiller, tractor causes soil erosion, water pumps, imbalance in ecosystems, sound pollution, imbalances of salts and minerals in soils. In such regular needs of farmers, nanomachines can be implemented for convenient working. Moreover, coupled with a decrease in the number of farmers, this has becomes a serious problem in agriculture. Large-scale farming machines are limited to large-scale farms, which only constitute a part of the crops. A valuable report indicates that Wearable-Agri-Robot can be used by an individual farmer. Agriculture labor involves the delicate work of pruning branches, judging the appropriate time for harvesting, etc. (Chu et al. 2005; Ghan and Kazerooni 2006; Steger et al. 2006; Toyama and Yamamoto 2009). In such Agri-Robot, microcomputer has been for control in the back, this robot is stand-alone. If it possible to implement nanomachines in such robotics, it may be also more convenient for farmer use. The Wearable-Agri-Robot shows to radish harvesting, cucumber harvesting, and fruit tree pruning (Toyama and Yamamoto 2009). Thus, nanomachines may be a helpful tool for the improvement sustainable agriculture.

10.18 Eco-friendly Agri-environment Developments

Agri-environment measures are a key element for the integration of environmental concerns into the Common Agricultural Policy. These can be designed to encourage farmers to protect and enhance the environment on their farmland by paying them for the provision of environmental services. Agri-environment measures play a crucial role for meeting society’s demand for environmental outcomes provided by agriculture. Extensive farming systems, a mosaic of landscapes, environmentally sound farming techniques adapted to region-specific needs, or extensive pasture systems are highly valued. Agri-environment payments encourage farmers to adopt agricultural activities or levels of production intensity that deliver positive environmental outcomes, while not being necessarily the first choice from the point of view of profitability. Examples of commitments covered by national/regional agri-environmental schemes are: (i) environmentally favorable intensification of farming; (ii) management of low-intensity pasture systems; (iii) integrated farm management and organic agriculture; (iv) preservation of landscape and historical features such as hedgerows, ditches and woods; (v) conservation of high-value habitats and their associated biodiversity.

Application of nanotechnology as an environmental impact can be split into two aspects: (i) the potential for nanotechnological innovations to help improve the environment and (ii) the possibly novel type of pollution that nanotechnological materials might cause if released into the environment (Crane and Scott 2012; Uskoković 2007). In the consequence of environmental pollution, nanopollution is a generic name for waste generated by nanodevices or during the nanomaterials manufacturing process. Ecotoxicological impacts of nanoparticles and the potential for bioaccumulation in plants and microorganisms is a subject of current research, as nanoparticles are considered to present novel environmental impacts (Karn et al. 2009; Stone et al. 2007; Valentini et al. 2013).

10.19 Organic Agriculture and Nanotechnology

An International Federation on Organic Agriculture Movements Position Paper on the Use of Nanotechnologies and Nanomaterials in Organic Agriculture rejected the use of nanotechnology in organic agriculture (BioFach 2011, Nuremberg, Germany; http://www.ifoam.bio/en/position-use-nanotechnologies-and-nanomaterials) explain that research has indicated that nanoparticles do not behave in a predictable manner and can be hazardous to life. A particular concern is the ability of nanomaterials to be directly taken up by individual cells and cell nuclei, where they can cause DNA mutation and even cell death. Despite these findings, nanomaterials are not currently subject to any specific safety testing, regulations or labeling in most places. However, Canada has banned nanotechnology in organic food production. An amendment was added to Canada's national organic rules banning nanotechnology as a "Prohibited Substance or Method" (http://www.non-gmoreport.com/articles/may10/canada_bans_nanotechnology_organics.php) (Sekhon 2014).

10.20 Food Nanotechnologies

A number of recent reports and reviews have identified the current and short-term projected applications of nanotechnologies for the food sector (Sekhon 2010). Food is nanofood when nanoparticles or nanotechnology techniques or tools are used during cultivation, production, processing, or packaging of the food. It does not mean

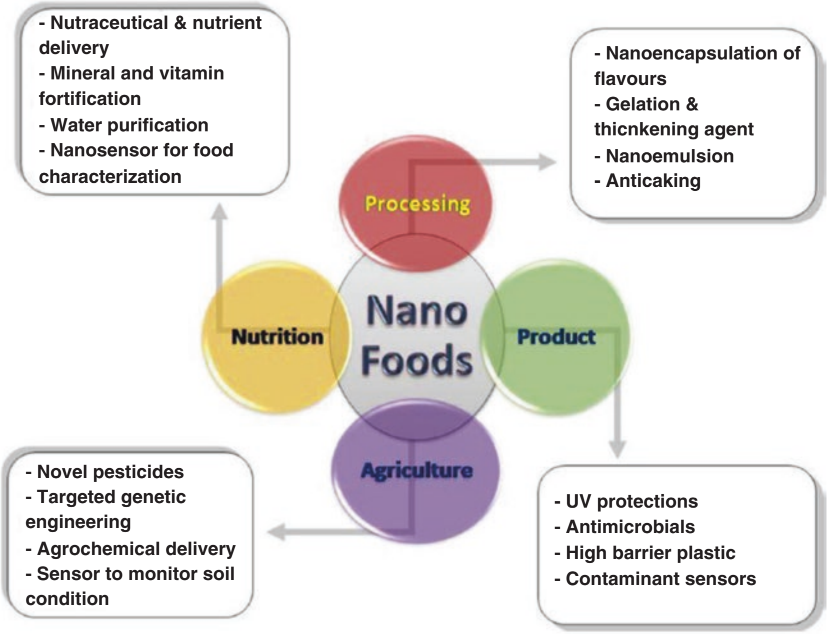

Fig. 10.9 Pictorial representation for some of the major applications of nanotechnology in different sectors of food and agriculture (Ranjan et al. 2014)

atomically modified food or food produced by nanomachines (Dasgupta et al. 2015; Ranjan et al. 2014; Sekhon 2010, 2014). Various applications of nanoparticles in the food industries are globally focused in (i) sensory improvements (flavor/color enhancement, texture modification), (ii) increased absorption and targeted delivery of nutrients and bioactive compounds, (iii) stabilization of active ingredients such as nutraceuticals in food structures, (iv) packaging and product innovation to increase shelf life, (v) sensors to assess the safety of food, (vi) as an antimicrobial against the food born pathogenic bacteria (Fig. 10.9) (Ranjan et al. 2014). Some food products containing nanoparticles present in the market are shown in Table 10.2.

10.21 Possibilities of Nanotechnologies in Agriculture

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. Nano-scale particles provide useful functions that are being rapidly explored in medicine, biotechnology, electronics, material science and energy sectors, among others (Parisi et al. 2015). While the food industry can be seen to be clearly benefiting from nanotechnology (in particular for food processing, distribution, packaging and functional food) (Ranjan et al. 2014; Sekhon

Table 10.2 Some food products containing nanoparticles present in the market are shown (Kumari and Yadav 2014)

Type of product	Product manufacturer	Nano content	Purpose
Nutritional supplement	Nanoceuticals "mycohydrin" powder RBC lifesciences	Molecular cages 1–5-nm diameter made from silica mineral hydride complex	Nanosized mycohydrin has increased potency and bioavailability. Exposure to moisture releases H^+ ions and act as powerful antioxidant
Nutritional drink	Oat chocolate nutritional drink mix, toddler health	300-nm particles of iron (sun active Fe)	Nanosized iron particles have increased reactivity and bioavailability
Food contact material	Nano silver cutting board, A–D Global	Nanoparticles of silver	Nanosized silver particles have increased antibacterial properties
Food packaging material	Adhesive for McDonald's burger containers, ecosynthetic	5–150-nm starch nanospheres	These nanoparticles have 400 times the surface area of natural starch particles. When used as an adhesive they require less water and thus less time and energy to dry
	Durethane KU2–2061 plastic wrapping, Bayer	Nanoparticles of silica in a polymer based nanocomposite	Nanoparticles in silica in the plastic prevent the penetration of oxygen and gas of the wrapping, extending the products shelf life
Food additives	Aquasol preservative, aquanova	Nanoscale micelle (capsule) of lipophilic or water insoluble substances	Surrounding active ingredients within soluble nanocapsules increases absorption within the body

2010, 2014), its real contribution to the agricultural sector is still uncertain. Overall, hopeful progress of other sectors also concern the agricultural sector, in which continuous innovation is strongly needed because of increasing global food security and climate change challenges. Over the last decades, overall progress are observed in area of crop production (plant protection products, fertilizers), soil improvement (water/liquid retention), water purification (water purification and pollutant remediation), diagnostic (nanosensors and diagnostic devices), plant breeding (plant genetic modification) and nanomaterials from plant (nanoparticles from plants). However, agri-nanotech innovative products are experiencing difficulties in reaching the market, making agriculture still a marginal sector for nanotechnology (Grobe and Rissanen 2012; Senjen 2012). This is due in particular to the high production costs of nanotech products, which are required in high volumes in the agricultural sector, unclear technical benefits and legislative uncertainties, as well as public opinion. Nevertheless, the R&D landscape is very promising and the possibilities offered by nanotechnology in several agricultural applications are being actively explored. Nanotechnology is progressing at rapid pace in other fields. The knowledge gained in other emerging sectors, such as energy and packaging, may over time be transferred, or may provide spill-overs, to agricultural applications as well (Parisi et al. 2015).

10.22 Risk Associations of Nanotechnology in Agri-food Production

Nanomaterials in agriculture and food are emerging issues of public and regulatory interest. In the arena of global food and livestock production, the main aspects of nanotechnology are improved quality and nutritional value. Despite of potential benefits that nanotechnology offers in the agri-food sector (grain cultivation, plant breeding, food production, feed for livestock, food ingredients, packaging, and nano-based smart systems), little is known on safety aspects of the application of nanotechnologies in food production and the incorporation of nanoparticles in food. Consumers also still lack knowledge about nanotechnology and possible risk association (Sekhon 2014). Risk-assessment procedures are not specific to agri-food nano-materials, resulting in uncertainty regarding the nature and extent of potential risks in most cases. Applications for nanomaterials currently used for meat, and food generally, include the use of nanoparticles and nanomaterials as food ingredients/additives that are placed directly into food or as a part of food packaging (Cushen et al. 2012; Dasgupta et al. 2015; de Oliveira et al. 2014; Mukhopadhyay 2014; Ranjan et al. 2014). The scientific community has identified a number of serious issues relating to risk assessments of nanomaterials such as the difficulty of characterising, detecting and measuring nanomaterials, as well as a lack of sufficient toxicology data. Apart from the scientific issues surrounding risk assessment, public acceptance of nanotechnology itself and nanofoods in particular continues to be elusive (Senjen 2012). Additionally, deficiencies were identified in characterization, detection and measurement of (engineered) nanomaterials in food and feed and biological matrices, as well as in the availability of information to toxicokinetics and toxicology, including optimal methods for testing of (engineered) nanomaterials (Grobe and Rissanen 2012). Thus, toxicity or risk assessment is essential step for nanomaterial prior to the implementation of sustainable growth of agriculture.

10.23 A Comparative Analysis of Indian Agriculture Systems with Agriculture Systems of Some Developed Countries

A constructive comparative analysis of present Indian agriculture systems with agriculture systems of some developed countries is an essential for implementation of modern technology for the sustainable growth of Indian agriculture sector in an ecofriendly manner. It has been seen that agriculture system and life of agriculturists in India are facing problems in day-to-day life due to number of basic problems such as lack of proper land maps, water irrigation systems, random selection and application of agriculture lands for housing complex, road, and transportation, destruction of natural forest for tourism, and political chaos. Lack of proper irrigation and drainage system is not only detrimental for farming but is also the cause for massive flood in the country.

Although India has major natural resources, including fertile lands, number of rivers and lakes, favorable climate, monsoon, intelligent man power, still India used to import a quite large number of agricultural products such as wheat, onion, edible oils and pulses, raw cashew nuts, tree nuts, fruit, etc (Downs et al. 2015; Nayyar and Sen 1994). Despite the overwhelming size of the agricultural sector, however, yields per hectare of crops in India are also generally low compared to international standards. Thus, we feel that improved land, water management, and public policy will enrich India's agriculture sectors. We had/have visited many villages in India and several developed countries, including Singapore, Germany, Japan, South Korea, USA, etc. We have observed that due to proper land, water management and public policy agriculture sectors of such countries are well developed compared with Indian agriculture sectors. Here, we like to emphasis on a particular agricultural problem, related to land reforms, a very basic but most important problem for the implementation of technology in Indian agriculture system.

Japan is good in sciences, technologies and researches; in addition Japan is also efficient in agriculture practices especially in rice agriculture. For example, Matsumoto is a small place in Nagano in Japan, where farmers cultivate grapes, apples, vegetables and paddy. Vast parts of lands are used for paddy cultivation. Lands are well connected with concrete irrigation systems for proper irrigation, and concrete pavements used for carrying saplings, soil ploughing machine, harvesting machine and agriculture products transportation. Every land is connected by water access gate, can get water in the field for rice cultivation and can keep land dry during rice harvesting, for potato, tomato and other vegetables cultivation. Indian farmer loose rice grains especially during harvesting time because harvested rice plants emerge in water for weeks because of water logging or unexpected raining during harvesting reason. Farmer carries harvested rice plants with rice grains in home and during this process farmer loose rice grains in fields and pavements. In Matsuomo, farmers harvest rice grains and package immediately in the field, carries rice grains and straw separately in good conditions.

In Matsumoto if any people like to see their land map can visit nearest city office where person can see their land map very easily. It has been observed in general that agriculture lands are well organized and separated from the normal housing complex or other industrial sectors. Due to efficient public policy and management, natural resources are not randomly used by general peoples. Thus, we suggest that reformation of land from a ground level; micro-scale is an essential step for the development and prosperity in the agriculture sector with the help of modern nanotechnology and sustainable agriculture practices.

Installation of irrigation systems or setting up industry requires land. While we were working with farmers in India for farming, land measurement, segmentation and making muddy pavement surrounding the farm lands, we saw that in many cases official land maps do not reconcile with the land occupied by owners, causing massive problem for installation irrigation systems, narrow concrete roads inside farmlands, installation of electric posts or setting up any industries. One land may have some known owners and many unknown owners, it is because there is no central approaches which can take care to update land map efficiently in regular basis. We were measuring farm lands with locally trained land measuring persons, who try to reconcile official land map with occupied land maps but in many cases we found inconsistent; whenever any organization or government agency or persons try to install any kind of systems for public welfare, there is no easy access for land maps from government officials because of lack of central approaches. We extended our observation from village of South Shibpur, Sundarban, West Bengal to other villages and saw exactly same problems, from these observation we hypothesis that official land maps and land occupied by owners are inconsistent throughout the India and in other under developed or developing countries which is main hindrance for setting up irrigation systems, concrete pavement for the improvement of agriculture practices and industry. In addition to this peace of many villages' perturbs due to unclear land maps, unclear land ownership and lack of easy access to land maps and official land measurement officials, causing conflicts among the farmers. Local people, land surveyors, farmers and officials try their best to solve land maps problems and ownership conflicts but because of lack of central approaches, neither villagers nor officials can clarify map complexities easily resulting in stagnant or delaying in many important developmental projects.

Thus, after brief comparison of farm sectors in developed countries and India, we propose following approaches in India to simplify map and land ownerships in order to ease access to installation of irrigation systems, concrete pavements, setting up industry and finally for improved agriculture practice to avail modern technologies for better farming. In laboratory scales, select randomly few small villages in Sundarbans and measure existing lands and compare with official maps, update ownerships and correct the land map wherever necessary. Once the land map and ownership is updated, design the map for concrete pavements, required irrigation systems and finally setup irrigation systems and concrete pavements. Designated person should be able to show the land map to farmers easily whenever necessary. Based on the research findings can setup irrigation systems throughout the country. In this way famers will able to use their land efficiently for only farming purposes. Many farmer families spend their whole life to solve land-related issues causing massive problem in country's development. We hope that the efficient land reformation from a ground level might be striking step towards the progressive development of Indian agricultures and life of agriculturist.

10.24 Conclusion

In the present review paper we have focused on the use of nanotechnology in sustainable agriculture with special emphasis in Indian agriculture systems. We reviewed conventional agriculture practices where we saw that global population is increasing and agriculture production is not adequate enough to support social need globally resulting in malnutrition, hunger, social instability, and death. Use of chemical fertilizer, insecticides, genetically modified organisms, and modern science and technology for agriculture increases production of agriculture products but there are big threat for ecosystems, risk for diseases, etc.

Next we assessed sustainable agriculture. We saw that systematic sustainable agriculture is not established in bigger scales. In many cases, farmers use fertilizers, insecticides, randomly without specification for specific crops which causes improper growth, heterogeneous crop production, and resistance to other crops. Use of bio fertilizer is not established properly yet. Bigger problem is that unorganized agriculture land, housing land. Establishing universal irrigation systems, transportation and storage facility are big challenges before application of sustainable agriculture in bigger scales. First step for application of nanotechnology in agriculture field is that organized irrigation systems, transportation, water conservation, storage facility, and connected post-harvest agriculture processing and food processing unit. Companies organize training for employees for specific jobs in regular basis and we suggest that agriculture experts should organize specific training program in regular basis to train farming communities.

Nanotechnology has been applied some agriculture fields including nanoagrochemicals, nanofertilizers, nanopesticides, water management, wastewater treatment, natural disaster management, drug delivery with nanotubes, plant genetics, disease, diagnosis, prevention, poultry farming (e.g. nanobiotic-Ag), aquaculture and fishery, nutraceuticals, drug delivery breeding of farm animals, etc. Risks of nanotechnology application in the agriculture and food processing have been also explained. Major agriculture in rural Indian area is affected due to lack of land rehabilitation and reformation where sustainability is far beyond to the public practices. Here, we have represented the present scenario of Indian agriculture system based on personal observation in Sundarbans, India and we have suggested possible application of (nano-) technology (Table 10.3).

Depending upon agricultural practices, it can hinder or sustain the ability to sustain the function of ecosystems to provide goods and services. To achieve success in sustainable agriculture and food processing, human resources also need sophisticated training and awareness (Mukhopadhyay 2014). Still application on nanotechnology in agriculture and food processing is under primitive stage and might take a few decades to move from laboratory to land and from land to human use, especially since it has to avoid the pitfalls experienced with ecosystem. The potential benefits of nanotechnology for agriculture, food, fisheries, and aquaculture need to be balanced against concerns for the soil, water, environment, and the occupational health of workers.

Table 10.3 Present Indian agriculture system. Conventional agriculture need to be transformed into sustainable agriculture for the progressive utilization of natural resources

Present agriculture practice	Proposal for Sustainable (nano-) agriculture practice
Unclear land maps and land ownerships	Clarification of land maps, land ownerships and maintain regular updated database for land maps and land owners
Lack of general public awareness about ecosystem and sustainable agriculture	Initiative for general public awareness about ecosystem and sustainable agriculture
Lack of efficient official access for redressal of land-related farmer issues such as land maps and land ownerships	Establishment of efficient official central access for redressal of farmer-related issues such as land maps and land ownerships
Lack of convenient pavements to connect main highway for transportation of farming equipment and farming products	Make convenient pavement for transportation of farming equipment and farming products
Lack of convenient irrigation systems for favorable farming	Set up irrigation systems, proper segmentation of land, installation of water access gate for each land for urgent use
Unorganized agriculture and housing land	Organization of technology friendly agriculture and housing land
Unorganized drainage systems and sluice gates cause water logging, flood and farming damage	Organized drainage systems and sluice gates to regulate optimal water level during rainy reasons and natural calamities to avoid farming damage
Wastage of farming products due to unorganized harvesting and post-harvest processing	Efficient harvesting, post-harvest processing, and storage systems
Saline water enters into farm land due to natural calamities and weak river/sea boundaries causing massive farming damage each year	Maintain river/sea boundaries regularly and possibly add concrete to boundaries.

In term Indian agriculture systems, application of sustainable agriculture is complex, as need proper land rehabilitation, land reformation, establishment of convenient pavement, eco-friendly convenient transportation system, water irrigation system, and after all general public awareness about their health, society and importance of ecosystem.

Finally, we have proposed small scale experiments for simplification of land maps and clarification of ownership, designing and setting up irrigation systems, pavement and agri-industry for sustainable agriculture.

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Index

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