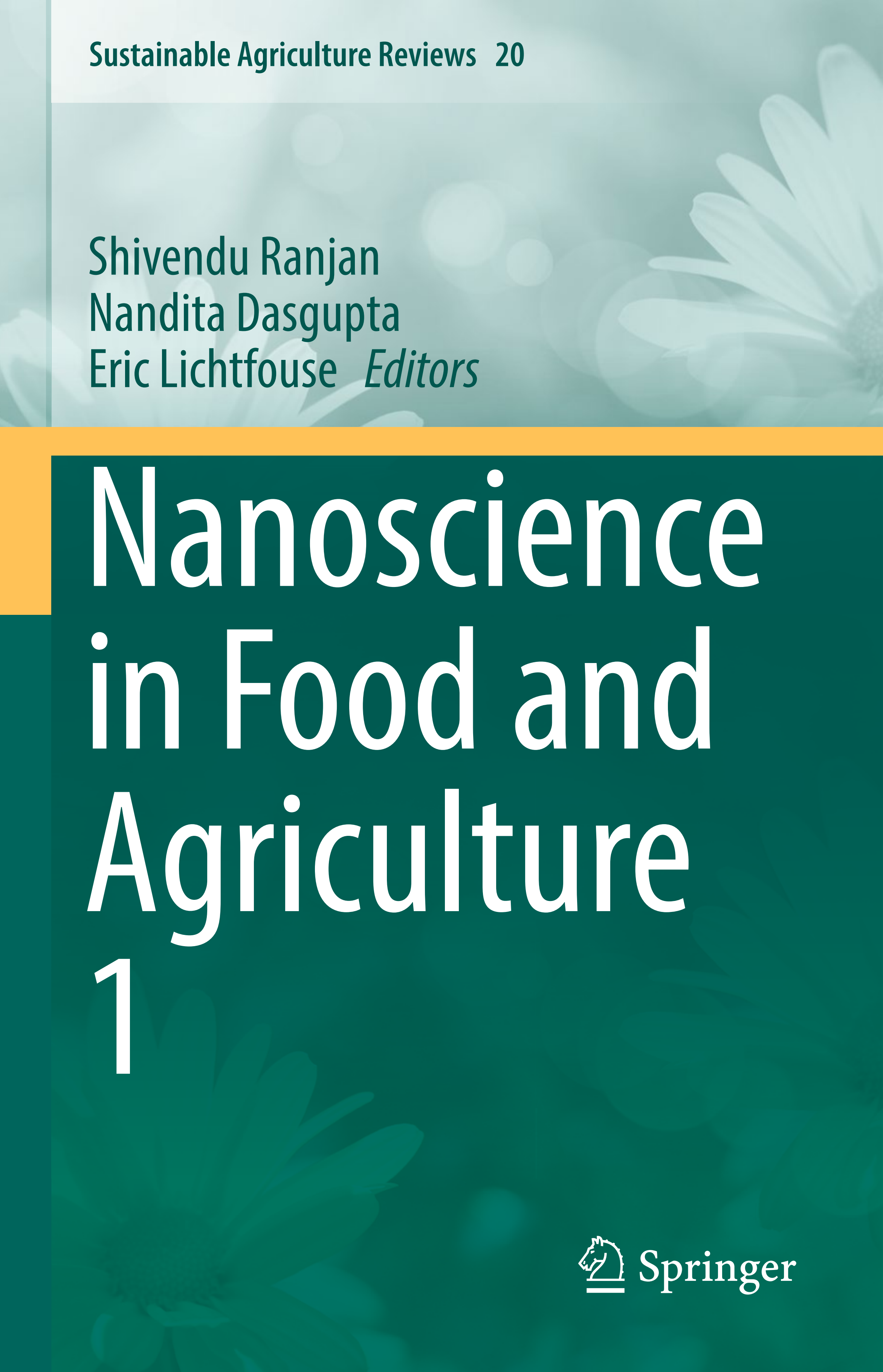
Sustainable Agriculture Reviews 20

Shivendu Ranjan
Nandita Dasgupta
Eric Lichtfouse *Editors*

Nanoscience in Food and Agriculture 1



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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 1

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We dedicate this book to our parents
–The Editors

There is plenty of room at the bottom
–Richard Feynman

Preface

This book is the first of several volumes on Nanoscience and Food in Agriculture, which will be published in series Sustainable Agriculture Reviews. Nanotechnology is a fast-evolving discipline that already produces outstanding basic knowledge and industrial applications for the benefit of society. Whereas the first applications of nanotechnology have been developed mainly in material sciences, applications in agriculture and food sectors are still emerging. Due to a rapid population growth, there is a need to produce food and beverages in a more efficient, safe and sustainable way. Here nanotechnology is a promising way to improve crop production, water quality, nutrition, packaging, and food security. There are actually a few comprehensive reviews and clear textbooks on nanotechnology in agriculture, water, and food. Therefore in this book we present ten chapters describing the synthesis and application of nanomaterials for health, food and agriculture. Applications to agriculture, food and water quality are symbolized in Fig. 1.

Definitions and an overall view of nanotechnology applications in agriculture, food, water and environment are described in the two first chapters by Dasgupta

Fig. 1 Nanotechnology will allow to improve the quality of water and food. *Left*: Roselette lake and Mont Blanc mountains, France (Copyright: G. Balvay/INRA 2015). *Right*: Ebly wheat rhubarb salad (Copyright: P. Libert/INRA 2015)

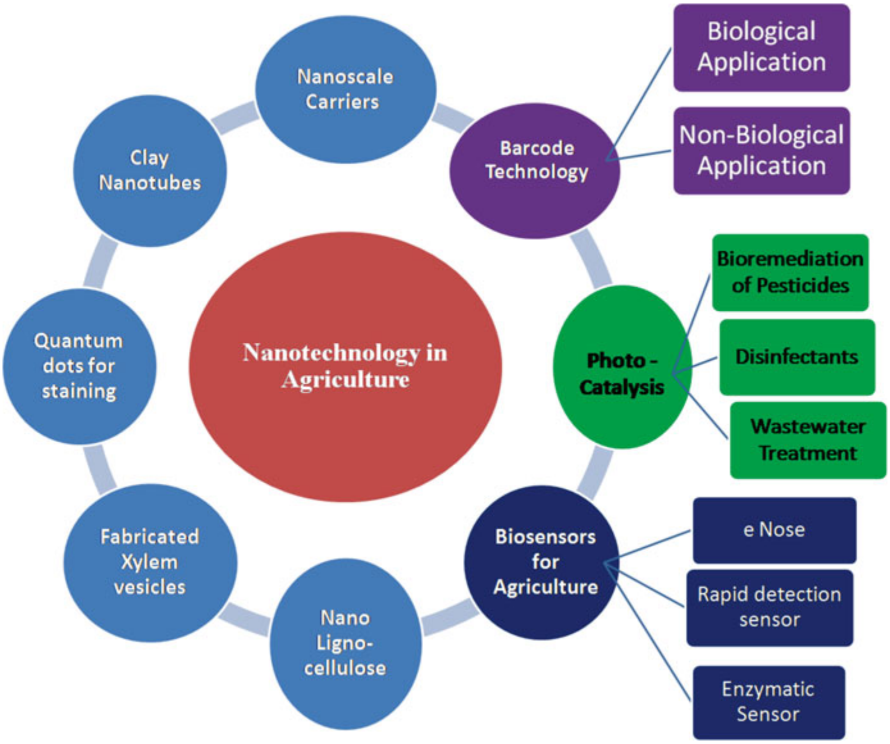

Fig. 2 Major applications of nanotechnology in agriculture. Dasgupta et al. Chap. 1

et al. and Singh (Fig. 2). Health and environmental applications of nanotechnology are presented in Chaps. 3, 4, and 5. Shukla and Iravani review green methods to synthesize metal nanoparticles and give applications to water purification in Chap. 3. The removal of up to 95 % of contaminants by nanoparticles, nanotubes and nanostructured membranes is described by Naghdi et al. in Chap. 4. Yoti et al. then review nanosensors for the detection of pathogenic bacteria in Chap. 5. Those nanosensors can be used as biodiagnostics to control food and water quality. Food applications of nanoscience are presented in Chaps. 6 and 7 by Kuswandi and Sarkar et al. Kuswandi explain in Chap. 6 that nanomaterials can improve packaging quality and that nanosensors can detect freshness and contaminants. The use of nanoparticles to protect ingredients such as vitamins, flavours and antimicrobials is reviewed by Sarkar et al. in Chap. 7.

Agricultural applications of nanotechnology are given in the last three chapters by Pulimi and Subramanian, Chhipa and Joshi, and Shalaby and El-Ramady. Pulimi and Subramanian explain in Chap. 8 that nanoclays, nanozeolites and nanominerals can be used as plant nutrient carriers, and to improve water retention in soils. They also describe the used of nanoparticles to improve classical methods of pollutant remediation such as phytoremediation and electrokinetic degradation. Chhipa and Joshi review the use of nanofertilisers, nanopesticides and nanosensors in agriculture in Chap. 9. Nanosensors are particularly useful in precision agriculture because they detect pests locally in real-time, which allow to treat them fast with minimal side-effects. In Chap. 10, Shalaby and El-Ramady reveal the benefits of zinc oxide and silicon nanofertilisers for plant growth.

Thanks for reading

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Contents

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His area of research is multidisciplinary whichare as 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 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 of 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 also serving as editorial board member and referee for reputed international peer reviewed journals. She has received Elsevier Certificate for "Outstanding Contribution" in reviewing from Elsevier, The Netherlands. She has also been nominated for Elsevier advisory panel for Elsevier, The Netherlands. She was the Guest Editor in 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,[2,3] 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

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the french-english newsletter Publier La Science.[7] He has published the book 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
Nanoagriculture and Water Quality Management

Nandita Dasgupta, Shivendu Ranjan, Arkadyuti Roy Chakraborty, Chidambaram Ramalingam, Rishi Shanker, and Ashutosh Kumar

Abstract Nanomaterials have rapidly gained importance in many fields of science and technology due to their unique properties. Nanomaterials are used in the agri-food sector notably for preservation and packaging, for agriculture and for water quality management. Future applications will improve shelf life, food quality, safety, and fortification. Nanosensors will be used to analyse contaminated food and water. Here we review the application of nanotechnology in agriculture and subdisciplines. The major points are the following. We explain the classification and synthesis of nanomaterials used for agriculture and water management. Then we present major applications such as nanoscale carriers, fabricated xylem vessels, nanolignocellulosic materials, clay nanotubes, photocatalysis, bioremediation of resistant pesticides, disinfectants, agricultural wastewater treatment, nanobarcode technology, quantum dots for staining bacteria, and nano-biosensors. Applications to water quality management include nanolignodynamic metallic particles, photocatalysis, desalination, removal of heavy metals, and wireless nanosensors.

Keywords Nanotechnology • Nanomaterials • Agriculture • Water quality management • Environment

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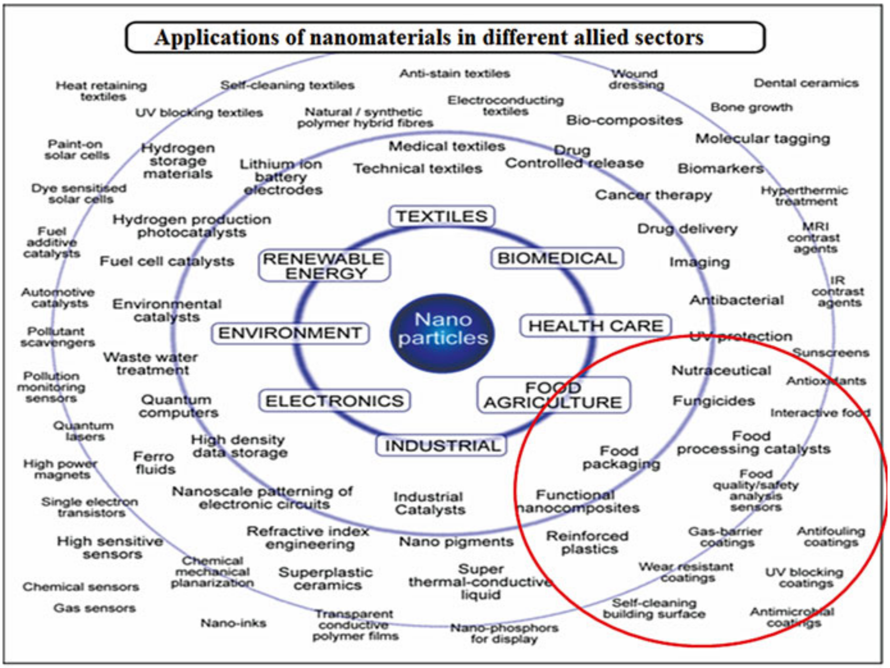
1.1 Introduction

The term ‘nano’ is coined from the Greek word for dwarf. A nanometre (nm) is 1-billionth of a metre, or approximately 100,000th of the width of a human hair. Nanotechnology has many applications in biotechnology and its allied field e.g. tissue engineering, drug delivery, biomedical engineering, food science and technology among others (Danie et al. 2013; Ranjan et al. 2014; Dasgupta et al. 2014). The applied nanotechnology has been shown in Fig. 1.1 using solar system model. A wide range of applications of nanotechnology is also emerged into the “agri-food sector” which includes the nanosensors, tracking devices, targeted delivery of required components, food safety, new product developments, precision processing, smart packaging and others, shown in Fig. 1.2 (Huang et al. 2010; McClements et al. 2009; Ranjan et al. 2014; Dasgupta et al. 2014). Nanotechnology can also improve the water solubility, thermal stability and bioavailability of the functional compounds of food (McClements et al. 2007, 2009; Miguel et al. 2014). Figures 1.3 and 1.4 represent the major applications of nanotechnology in food processing and packaging, the same has already been discussed in many review articles earlier, by Ranjan et al. (2014) and Dasgupta et al. (2014).



Source: http:// luratia.com/nano

Fig. 1.1 Solar system model showing applications of nanotechnology in different allied sectors including industrial, electronics, environment, renewable energy, textiles, biomedical, healthcare, foods, agriculture and agro-foods. The *red-circled* part has been covered in this chapter (Courtesy: www.lurasia.com/nano and www.xpertarena.com)

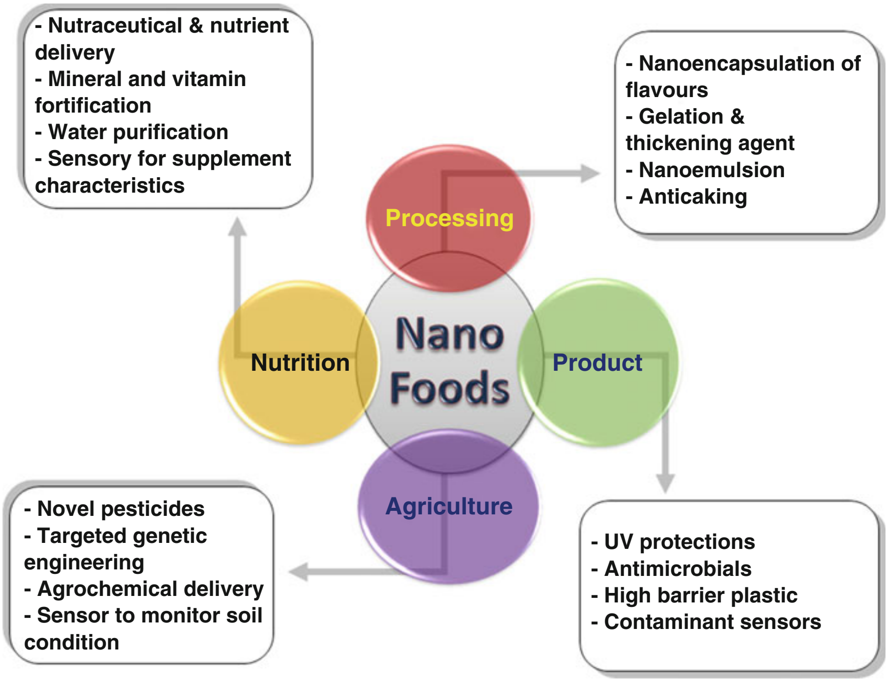


Fig. 1.2 A mind-map showing the linkage of nano-foods with agriculture, nutritional, process development and product development. Pictorial representation for some of the major applications of nanotechnology in different sectors of food and agriculture (Courtesy: Ranjan et al. 2014)

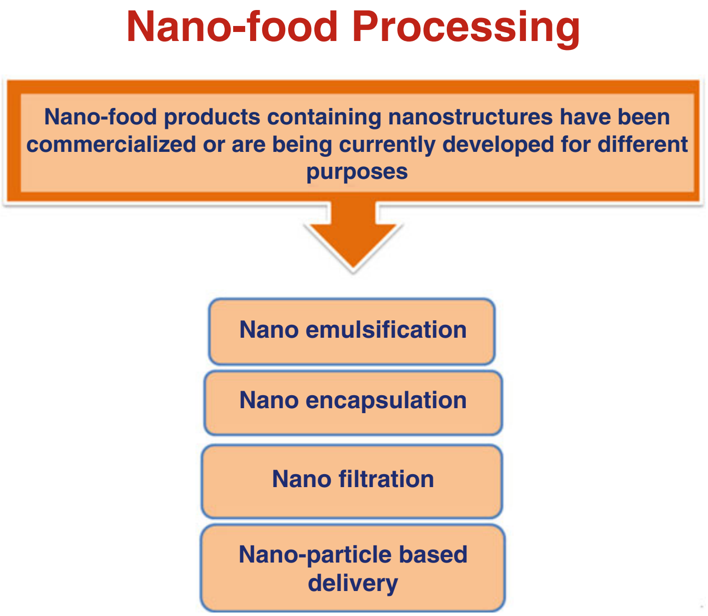


Fig. 1.3 Major types of nano-structures or processes which are being used to develop nano-foods to be launched in market

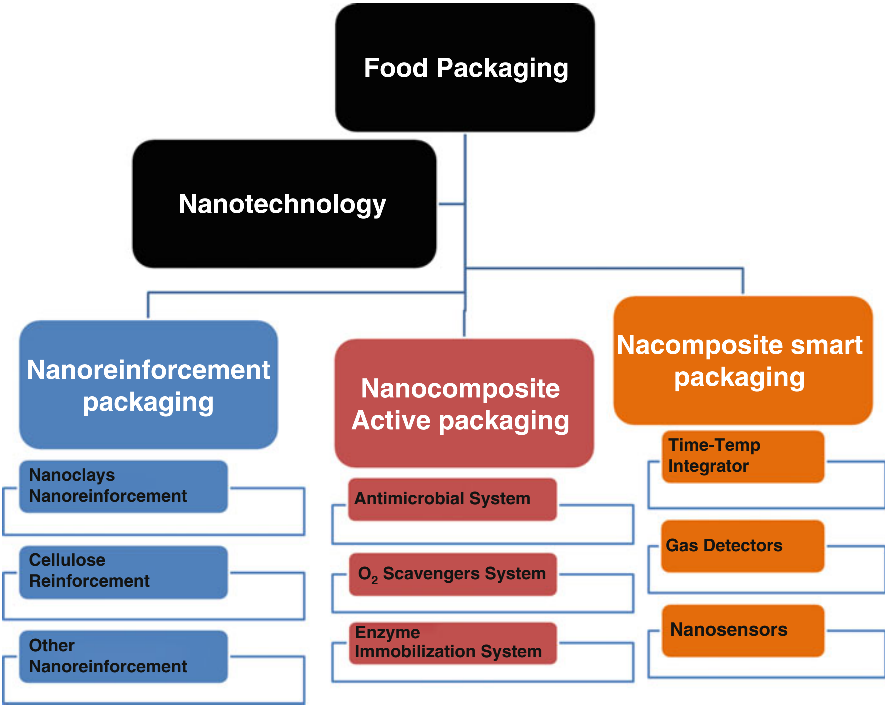


Fig. 1.4 Pictorial representation to sumamrize the different types and sub-types of nano-food-packaging being used along with their different applications (Courtesy: Ranjan et al. 2014)

Agricultural products influence most aspects of life, including everyday materials, such as fuels, textiles, furniture, feedstock for bio-based products including food and feed. Technology advancement is needed to achieve the future global needs from agriculture. Nanoscience and nanotechnology has shown great potential in improving food safety, quality, product traceability, nutrient delivery, enhancing packaging performance, and improving agricultural and food processing. In the present review an attempt has been made to summarize the classification and the synthesis method for the nanomaterials used in agricultural practices and water quality management. Also, the application of nanomaterials in the agriculture such as nanoscale carriers, fabricated xylem vessels, nanolignocellulosic materials, clay nanotubes, photo-catalysis, bioremediation of resistant pesticides, disinfectants, agricultural wastewater treatment, nanobarcode technology, quantum dots for staining bacteria, different types of nano-biosensors along with the current research trends, future directions, opportunities and research gaps in this field has been discussed in detail. The goal of this article is to provide the perspectives of researchers working with nanotechnology to address agricultural and water quality management problems.

1.2 Classification of Nanomaterials

Nanomaterials can be classified as (i) nanoparticles (ii) nanoclays and (iii) nanoemulsions, which can be synthesized by a number of methods and have many applications in agri-food sector.

1.2.1 Nanoparticles

Nanoparticles can be categorized into different types based on their ability to carry different reactions with different ingredients and environmental conditions. Depending on the chemical characteristics, Nanoparticles can also be divided into two broad categories- organic and inorganic.

Organic Nanoparticle-sometimes referred to as nanocapsules, when used to enhance the bioavailability of nutrient and their delivery. However, seen from a general level, they can be defined as nano-vesicular systems that exhibit a typical core-shell structure in which the drug is confined to a reservoir or within a cavity surrounded by a polymer membrane or coating (Anton et al. 2008). There are six classical methods for the preparation of nanocapsules: nanoprecipitation, emulsion-diffusion, double emulsification, emulsion-coacervation, polymer-coating and layer by-layer (Mora-Huertas et al. 2010) as mentioned in Table 1.1. Recently a new class of water-soluble red fluorescent organic nanoparticles have been prepared for an application in cell imaging which further can be used in the development of nanosensors (Xiqi et al. 2014). Also, a fluorescent organic nanoparticle has been developed by Zhang et al. (2014) with dye removal (remediation) from soil as well as and water. This facilely incorporated polymeric nanoparticle showed high water dispersibility, uniform size, strong red fluorescence and excellent biocompatibility, which makes them promising in water purification, nano-sensor development for water as well as agricultural products (Zhang et al. 2014).

1.2.1.1 Inorganic Nanoparticles

Inorganic ingredients manufactured at the nanoscale with variations of compounds and approved for use in food, e.g. titanium dioxide, a food colorant, can be used as a UV protection barrier in food packaging when used as a nanoparticle. New storage containers/utensils (food contact materials) based on embedded inorganic nanoparticle have been designed for preservation of prepared agricultural products. Grain storage bins are being produced with silver nanoparticle embedded in the plastic for killing bacteria from any food that was previously stored in the bins and minimizing health risks (Food Safety Authority of Ireland 2008). A cellulose-based bactericidal nanocomposites containing silver nanoparticle have been developed, which

Table 1.1 Upstream and downstream procedures for the preparation of nanocapsules (Mora-Huertas et al. 2010)

S. No.	Upstream process for nanocapsule formation	Downstream process for nanocapsule concentration, purification and stabilization
1	**Nanoprecipitation Method** ➢ Organic phase is slowly injected (dropwise and moderate stirring) to the aqueous phase	**Solvent Elimination** ➢ Moderate magnetic agitation ➢ Evaporation by vacuum ➢ Tangential ultrafiltration **Purification** ➢ Water washing ➢ Diafiltration ➢ Filtration through 0.45µm ➢ Gel filtration **Recuperation** ➢ Ultrasonication **Stabilization** ➢ Spray drying ➢ Lyophilization/freeze drying
2	**Emulsification-diffusion Method** ➢ Organic and aqueous phase are emulsified (high shear mixture) ➢ Diffused (moderate stirring) to dilution phase	
3	**Emulsification-coacervation Method** ➢ Organic and aqueous phase are emulsified (mechanical stirring or sonication) ➢ Coacervation (moderate stirring) in the presence of crosslinking agents or dehydratant agent	
4	**Double emulsification Method (Water-Oil-Water)** ➢ Organic phase and first Aqueous phase are emulsified in water-oil system (sonication) ➢ Second aqueous phase and previous solution are emulsified in oil water system (high shear mixture)	
5	**Polymer coating Method (Water-Oil-Water)** ➢ Organic and aqueous phase are emulsified in water-oil system (sonication) ➢ Second phase i.e. coating agent and previous solution are emulsified in oil water system (sonication or high shear mixture)	
6	**Layer by layer** ➢ Template will be encapsulated with several layers of mixture of anionic/cationic polymers and coat charged polymer	

exhibited an improved bactericidal and nanocomposite properties. Further it has been concluded that these properties may have the future applications in active packaging of food and agricultural products (Márcia et al. 2012). Also, silver nanoparticle incorporated into carboxymethylcellulose films have been studied for its antimicrobial studies for food and agricultural products packaging and found suitable for the same (Siqueira et al. 2014). The detailed view on packaging of agricultural and food product is provided by Ranjan et al. (2014) and Dasgupta et al. (2014).

Similar to organic, inorganic nanoparticles are also having several methods of production e.g. gas and liquid phase synthesis method, which are further classified into different methods. Gas phase synthesis methods have mainly three types for synthesis (a) flamed spray synthesis (b) laser induced gas evaporation method synthesis (c) plasma based synthesis. However, liquid phase inorganic nanoparticles synthesis methods may further categorized into (a) co-precipitation method and (b) sol-gel approach (Food Safety Authority of Ireland 2008). The properties of nanoparticles have shown to be dependent on the size and other surface properties, which ultimately depend on the synthesis procedure. Hence, it is necessary to understand the synthesis procedures of nanoparticles for their specific application. The detailed overview of inorganic nanoparticles synthesis has been given in the book of Jesus et al. (2012), which has been summarized below for better understanding.

1.2.1.2 Flame Spray Synthesis

Three large scale commodities have been around for half a century which are pigmentary titania (white pigment), aerosol-made silica and carbon black (tire soot) are made by flame processes at several megatons per year (Layman 1995; Ulrich 1984). Production of these materials started in the 1940s. In principle, it would appear attractive to extend this apparently useful flame processes to other materials (Stark et al. 2002). Flame-made oxides have been explored for applications as sensors which further can be used in agricultural field (Athanassiou et al. 2006). As a result, a number of products have become available in the form of nanoparticles, such as nano-gypsum (Osterwalder et al. 2007), nano-salt (Grass and Stark 2005) and nano-tricalcium phosphate (Maciejewski et al. 2008). Further adaptations within the flame spray synthesis technology gives access to the production of metal nanoparticles (Athanassiou et al. 2006; Grass and Stark 2006). This is achieved by a modification of the flame reactor operating under reducing (oxygen starved) conditions (Grass and Stark 2006). Very recently, one further step was taken and the controlled deposition of carbon on the metal surface of nanoparticle also became accessible (Athanassiou et al. 2006, 2007). For example, the suitability of carbon coated copper nanoparticles in water based dispersions or inks of such have been shown to offer a simple production method to highly sensitive humidity sensor coatings (Luechinger et al. 2007). In summary, flame spray synthesis allows the scalable fabrication of most accurate mixed oxide compositions, salt, metal and carbon-coated metal or silica-coated metal oxide nanoparticle (Teleki et al. 2008) based on metal loaded liquid precursors.

1.2.1.3 Laser Induced Gas Evaporation Method

Instead of combustion of a liquid precursor giving access to oxidic nanoparticles, Kato (1976) produce a range of different ultrafine refractory oxides (SiO_2, MgO, Al_2O_3, Fe_3O_4, Mg_2SiO_4, $CaTiO_3$ and $MgAl_2O_4$) by the use of a CO_2 laser. The laser was used to vaporize starting material in form of powder or sintered or fused blocks. The vaporized material condensed in an environment of inactive gases and resulted in nanoparticles of around 10 nm particle diameter at a production rate of 10 mg/min (0.6 g/h). Ullmann et al. (2002) studied the systematic influence of the operating parameters on laser ablation for the aerosol generation and concluded that laser ablation is a convenient method for laboratory scale nanoparticles generation.

1.2.1.4 Plasma Based Nanoparticles Production

A similar method to laser induced gas evaporation are plasma reactors. In this case plasma delivers the energy necessary to evaporate the starting materials of various types including gases, liquids and solids. At temperatures of around 10,000 °C the plasma generates reactive ions and radicals. During the pull-out from the plasma region the temperature of the gas drops and nanoparticles are formed (Young and Pfender 1985). Plasma based methods have been used to synthesize nanoparticles in form of metal oxides (Suzuki et al. 2001), metals (Jiang and Yatsui 1998) or metal nitrides (Kinemuchi et al. 2003).

1.2.1.5 Co-precipitation Method

In a first step of a typical co-precipitation reaction, the conditions are adjusted to maximize the simultaneous generation of sparingly soluble particles. The key properties of the final product (above all particle size and morphology) are subsequently determined in secondary processes such as aggregation or Ostwald ripening. In the final step, the as-formed particles are usually thermally decomposed to oxides. An advantage of the co-precipitation method is that particle sizes can be well controlled for the fabrication of monodisperse inorganic nanoparticles possible. A major disadvantage though is the involvement of vast amounts of solvents and surfactants (Cushing et al. 2004).

1.2.1.6 Sol-Gel Method for Inorganic Nanoparticles Synthesis

Another inorganic nanoparticles synthesis method based on liquid precursors is the processing of materials by the *sol-gel* method. This process dates back to the mid 1800s where scientists found that they were able to synthesize ceramic or glassy material from a viscous gel. Typically, metal alkoxides or metal chlorides are used as starting materials forming the solvated metal precursor (the *sol*). This precursor undergoes hydrolysis and polycondensation reactions to form a gelated colloid (the *gel*). The reactions of this oxide- or alcohol-bridged network continue until the gel transforms into a solid mass under expulsion of the solvent from the pores. Subsequently, the monolith is calcined at temperatures up to 800 °C. In the firing step when the temperature rises above 800 °C densification and decomposition of the gel occurs under collapse of the gel network. The sol-gel process is ideally suited for the fabrication of synthetic zeolites, where a porous “open” structure is desired for the accommodation of a wide variety of cations (Hench and West 1990).

1.2.2 Nanoclays

They are naturally occurring aluminium silicate, primarily composed of fine-grained minerals having sheet-like geometry. The sheet-structured hydrous silicates are generally referred to as phyllosilicates. They are inexpensive and eco-friendly materials and have been found for multifarious application. These clay minerals have been widely studied in practical applications such as in geology, agriculture, construction, engineering, process industries, and environmental applications. They provide an attractive alternative for the decontamination of soils, underground waters, sediments and industrial effluents i.e. in the field of water purification and recently nanoclays have been found to have application in sensor development (Garrido-Ramirez et al. 2010; Grasielli et al. 2012). The most studied nanoclayis montmorillonite (MMT), whose chemical general formula is $Mx(Al_4\text{-}xMgx)\ Si_8O_{20}(OH)_4$. montmorillonite is a representative of 2:1 layered *phyllosilicates*, whose platelets have two layers of tetrahedral silica sheets filled with a central octahedral alumina sheet (Weiss et al. 2006). This kind of clay has a moderate negative surface charge that is important to define the interlayer spacing (Xin-Juan et al. 2015). The imbalance of the surface negative charges is compensated by exchangeable cations (typically Na^+ and Ca^{2+}). The parallel layers are linked together by weak electrostatic forces (Tan et al. 2008). Montmorillonite is excellent reinforcing filler, due to its high surface area and large aspect ratio, which ranges from 50 to 1000 (Uyama et al. 2003). The improved barrier properties of polymer-clay nanocomposites seem to be due to an increased tortuosity of the diffusive path for permeants, forcing them to travel a longer path to diffuse through the film. The increase in path length is a function of the aspect ratio of the clay and the volume fraction of the filler in the composite. This theory was developed by (Nielsen 1967) and was further corroborated by other authors (Mirzadeh and Kokabi 2007; Adame and Beall 2009). Clays have also been reported to improve the mechanical strength of biopolymers (Cyras et al. 2008), although they may decrease polymerelongation (Petersson and Oksman 2006).

Recently many applications have been found using montmorillonite and/or incorporating/modifying montmorillonite using several techniques. Gholam et al. (2013) have been found the increased adsorption rate and more nanocomposite strength when modified montmorillonite based nanoclay – further the application of which was found for water purification by removal of crystal violet dye. Hydrogel nanocomposites were synthesized from grafting of acrylamide onto hydroxypropyl methylcellulose using methylenebisacrylamide cross linker and sodium montmorillonite (Na-MMT) nanoclay. The investigation of the dye adsorption capacity and rate of nanocomposite hydrogels as a function of Na-MMT content revealed that the both adsorption capacity and rate is enhanced as the nanoclay content is increased in nanocomposite composition (Gholam et al. 2013). Soy protein hydrogels with intercalated montmorillonite nanoclay bound with transglutaminase cross-linking shows enhanced elastic properties. This intercalated soy proteins with montmorillonite can be used to manufacture biodegradable nanocomposite materials with improved functional performances further application of which is food and agricultural products packaging (Jin and Zhong 2013). A nanofilm have been developed by novel dispersion method using gum exudates from Brea tree and nanoclayparticles (montmorillonite) and characterized – the main properties of this biofilm are improved water barrier capacity, reduced film permeability and reduced permselectivity for gases. These properties of this (montmorillonite nanoclay based biofilm) gives ample scope for its application for packaging as well as preservation of agricultural products (Aníbal et al. 2014). Montmorillonite nanoclay has been found application in biosensor development as well. Grasielli et al. (2012) have developed a novel atemoya biosensor for glyphosate determination which was based on the inhibitor effect of the pesticide on enzymatic activity. The peroxidase enzyme was immobilised on nanoclay based on montmorillonite modified (Grasielli et al. 2012). Other than montmorillonite a novel polyvinylidene fluoride (PVDF)/NC hollow fibre membranes were fabricated by non-solvent induced phase separation (NIPS) to study the improvement of membrane physical endurance. PVDF membranes containing commercial nanoparticles are therefore promising for improved abrasion resistance in water treatment applications (Yan et al. 2014).

1.2.3 Nanoemulsions

Nanoemulsion consists of a lipid phase dispersed in an aqueous continuous phase, with each oil droplet being surrounded by a thin interfacial layer consisting of emulsifier molecules (Acosta 2009; McClements et al. 2007; Nicolas et al. 2014). Usually, nanoemulsions are highly stable to gravitational separation because the relatively small particle size means that Brownian motion effects dominate gravitational forces. They also have good stability against droplet aggregation because the range of attractive forces acting between the droplets decreases with decreasing particle size, while the range of steric repulsion is less dependent on particle size (Tadros et al. 2004; Siti et al. 2013).

Other than increasing bioavailability (Hira et al. 2014) and antioxidant (Dasgupta et al. 2015) the bactericidal (Vijayalakshmi et al. 2013), antimicrobial (Karthikeyan et al. 2012; Dasgupta et al. 2015), antihelminthc (Karthikeyan et al. 2011), insecticidal (Megha et al. 2014) properties of nanoemulsion gave it importance to be used in agriculture – mainly to increase the shelf life of agricultural products and water quality management (Ranjan et al. 2014; Dasgupta et al. 2014). Chaw et al. (2013) have formulated a nanoemulsion with the insecticidal and pesticidal activity. The green nanoemulsion – laden glyphosate isopropylamine – formulated were able to suppress creeping foxglove (*A. gangetica*), slender button weed (*D. ocimifolia*) and buffalo grass (*P. conjugatum*). This initial discovery could be the platform for developing better penetration of agrochemical formulations in the future (Chaw et al. 2013). Similarly they have again used the same nanoemulsion with slight modification as a herbicide and have concluded that it is having controlling ability for *Eleusine indica* (Chaw et al. 2012). Recently many authors have given hypothesis that the microbial products can be used as natural emulsifier to have safer nanoemulsion to be used in the field of agro-food products (Shivendu et al. 2014;

Vanaja et al. 2014). Also many have hypothesized that the plant extracts or natural products could be more efficient for its activity when the same can be used in the form of nanoemulsions (Nandita et al. 2014, 2015b, c). To understand the activity of nanoemulsion, it is mandatory to understand the synthesis procedures. Also, to get better bioactivity, the understanding of the bioactive components retention with nanoemulsion should also be understood.

1.2.3.1 Production of Nanoemulsion

Nanoemulsion can be produced using a variety of methods, which are classified as either high-energy or low energy approaches (Acosta 2009; Leong et al. 2009; Tadros et al. 2004; Koroleva and Evgenii 2012; Silva et al. 2012).

High-energy approaches revolve around the use of mechanical force to generate intense disruptive forces that breakup the oil and water phases thereby forming oil droplets. For example, high-pressure valve homogenisers, micro-fluidizers, and sonication methods (Leong et al. 2009; Wooster et al. 2008). The production of nanoemulsions via this method is primarily governed by composition i.e. mainly surfactants, functional compounds and secondarily by the quantity of energy applied. Hence these emulsions depict a tendency towards preserving their formation against formulation modification like addition of monomer, surfactant, co-surfactant etc. (Anton et al. 2008). High energy approach for production of nanoemulsionis further classified into high pressure homogenization, Ultrasound approach (Quintanilla-Carvajal et al. 2010) and high speed devices approach (Anton et al. 2008).

1.2.3.2 High-Pressure Homogenization

The mixture is exposed to very high pressures and is pumped through a restrictive valve. The very high shear stress causes the formation of very fine emulsion droplets (Quintanilla-Carvajal et al. 2010). Further the impact of homogenization on design and structure of nanoemulsion have been described by Finke et al. (2014). Nanoemulsions with antimicrobial/microbial inactivation property have been developed by high-pressure homogenization method. This formulation can be further applied for increasing shelf life of agricultural products and also can be used in water quality management by decreasing microbial load of the water (Francesco et al. 2013).

1.2.3.3 Ultrasound

When two immiscible liquids are submitted to high-frequency sound waves in the presence of a surfactant, emulsion droplets are formed by cavitation. This causes intense shock waves in the surrounding liquid and the formation of liquid jets at high speed is responsible for the formation of emulsion droplets. However, this technology has not yet been efficiently used for industrial-scale applications (Maa and Hsu 1999; Quintanilla-Carvajal et al. 2010; Sanguansri and Augustin 2006). The scaled up process fornanoemulsion formulation at industrial level by ultrasound method have been described by using continuous-flow production method – which can be further applied for formulating nanoemulsion for agricultural applications (Alexey and Simon 2014). Shams and Ahi (2013) have developed 5A zeolite nanocrystals using kaolin via nanoemulsion by ultrasonic technique with a increased sorption properties which can further be used in water quality management for remediating the sludge (Shams and Ahi 2013).

1.2.3.4 High-Speed Devices

Rotor/stator devices (such as Ultra-Turrax) when compared with the other high energy approaches do not provide a good dispersion in terms of droplet sizes. With the energy provided mostly being dissipated as generating heat. Stable nanoemulsions are difficult to obtain (Anton et al. 2008; Walstra 1993). Francesco et al. (2012) have increased the antimicrobial delivery system of nanoemulsion when designed by high-speed devices (Ultra-Turrax) and proper emulsifier. Same method can be used to develop nanoemulsions with improved activities which can be applied in the field of agriculture and water quality management.

Low energy approaches rest upon the impromptu formation of oil droplets within mixed oil-water-emulsifier systems as and when solution conditions are altered, e.g., phase inversion and solvent demixing methods (Anton et al. 2008; Yin et al. 2009). Nanoemulsions are obtained in response to phase transitions during emulsification at constant temperature and altered composition (Usón et al. 2004) or vice versa (Morales et al. 2003). Low energy approaches are further classified into membrane emulsification (Sanguansri and Augustin 2006), spontaneous emulsification (Anton et al. 2008), solvent displacement (Yin et al. 2009), emulsion inversion point (Sadtler et al. 2010) and phase inversion point (Sadurní et al. 2005).

1.2.3.5 Membrane Emulsification

It is a low-energy process that requires less surfactant (when compared with high energy methods) and produces emulsions with a narrow size distribution range. This method involves formation of a dispersed phase (droplets) through a membrane into a continuous phase. Nevertheless, this method has as limitation the ‘low flux’ of the dispersed phase through the membrane, this being an issue during scale-up (Sanguansri and Augustin 2006). Membrane emulsification mainly used to increase the bioavailability of the nutrients e.g. vitamine E (Abdallah et al. 2012; Dasgupta et al. 2015). Many nanoemulsions have been formulated (by membrane emulsification) to increase the shelf life of post harvested products (Ghosh et al. 2014). Some nanoemulsions have been formulated by this method with improved bioactivity (Joseph and Heike 2014) and also which acts as a carrier to deliver some bioactive compound and/or compounds (Keun et al. 2012). In the same way some nanoemulsion should be discovered/identified which can be used as a carrier either in plant tissues or at soil/water/plant interface; also some nanoemulsion conjugated with the compounds needed for plant growth and can increase the bioavailability of it should be researched.

1.2.3.6 Spontaneous Emulsification

This mechanism occurs when an organic phase and an aqueous phase are mixed, with the organic phase being a homogeneous solution of oil, lipophilic surfactant and water-miscible solvent, and the aqueous phase consisting of water and hydrophilic surfactant (Bouchemal et al. 2004). Spontaneous emulsification is produced by different mechanisms (e.g. diffusion of solutes between two phases, interfacial turbulence, surface tension gradient, dispersion mechanism, condensation mechanism) which seem to be affected by the systems' compositions and their physicochemical characteristics like the physical properties of the oily phase and nature of the surfactants (Bouchemal et al. 2004). This process itself increases entropy and thus decreases the Gibbs free energy of the system (Anton et al. 2008).

1.2.3.7 Solvent Displacement

This method consists of mixing a water-miscible organic solvent containing lipophilic functional compounds in an aqueous phase containing an emulsifier. The rapid diffusion of the organic solvent in the aqueous phase promotes the formation of nanoemulsions enabling their preparation in one step at low-energy input with high yield of encapsulation. Finally, the organic solvent is removed from the nanodispersion under reduced pressure. Nevertheless the use of this technique is limited to water-miscible solvents (Yin et al. 2009). The non soluble compounds can be made available by using this method of nanoemulsion fabrication (Regina et al. 2007; Kyle et al. 2014; Gabriel and David 2015) – thus solvent displacement method can be used in those agricultural soils in which some of the compounds are unavailable because of its poor solubility.

1.2.3.8 Emulsion Inversion and Phase Inversion Point

It involves variation of system composition at a constant temperature. The structures are formed through a progressive dilution with water or oil in order to create kinetically stable nanoemulsions (Anton et al. 2008; Sadtler et al. 2010). Phase inversion point method uses the specific ability of surfactants (non-ionic) to alter their affinities to water and oil in function of temperature at a fixed composition. It consists in suddenly breaking-up the micro-emulsions maintained at the phase inversion point by a rapid cooling (Izquierdo et al. 2004; Sadurní et al. 2005) or by a dilution in water or oil (Anton et al. 2008). Nanoemulsions immediately formed are kinetically stable and can be considered as irreversible. This process is relatively simple, prevents the encapsulated drug being degraded during processing, consumes low amounts of energy and allows an easy industrial scale-up (Anton et al. 2008). Emulsion inversion and phase inversion methods are used to control the droplet size and stability of nanoemulsion (Felix et al. 2012). For nanoemulsion research for agricultural applications these two methods should also be analyzed.

1.3 Nanotechnology and Research Trends in Agriculture

Currently, the major challenges faced by world agriculture include changing climate, urbanization, sustainable use of natural resources and environmental issues like runoff and accumulation of pesticides and fertilizers. These problems are further intensified by an alarming increase in food demand that will be needed to feed an estimated population of six to nine billion by 2050 (Chen and Yada 2011). This above-mentioned scenario of a rapidly developing and complex agricultural system exists and greater challenges will be posed to the developing countries as, in the developing countries, agriculture is the backbone of the national economy.

Nanotechnology, this vast field of the twenty-first century, is making a very significant impact on the world's economy, industry and people's lives (Gruere et al. 2011; Scott and Chen 2003). Applications of nanotechnology in materials science and biomass conversion technologies applied in agriculture are the basis of providing food, feed, fibre, fire and fuels. Through advancement in nanotechnology, a number of state-of-the-art techniques are available for the improvement of precision farming practices that will allow precise control at nanometer scale (Fig. 1.5). Nanotechnology can also be an alternative source of fertilizer. In an experiment, it was observed that SiO_2 Nanoparticles enhanced germination in tomato (*Lycopersicum esculentum*) seeds (Manzer and Mohamed 2014).

1.3.1 Nanoscale Carriers

Nanoscale carriers can be utilized for the efficient delivery of fertilizers, pesticides, herbicides, plant growth regulators etc. The mechanisms involved in the efficient delivery, better storage and controlled release include: encapsulation and entrapment, polymers and dendrimers, surface ionic and weak bond attachments among others. These mechanisms help improve stability against degradation in the environment and ultimately reduce the mass/amount to be applied, which reduces chemical runoff and alleviates environmental problems. These carriers can be designed in such a way that they can anchor the plant roots to the surrounding soil structure and organic matter. This can only be possible through the molecular and conformational mechanisms between the delivery nanoscale structure and targeted structures and

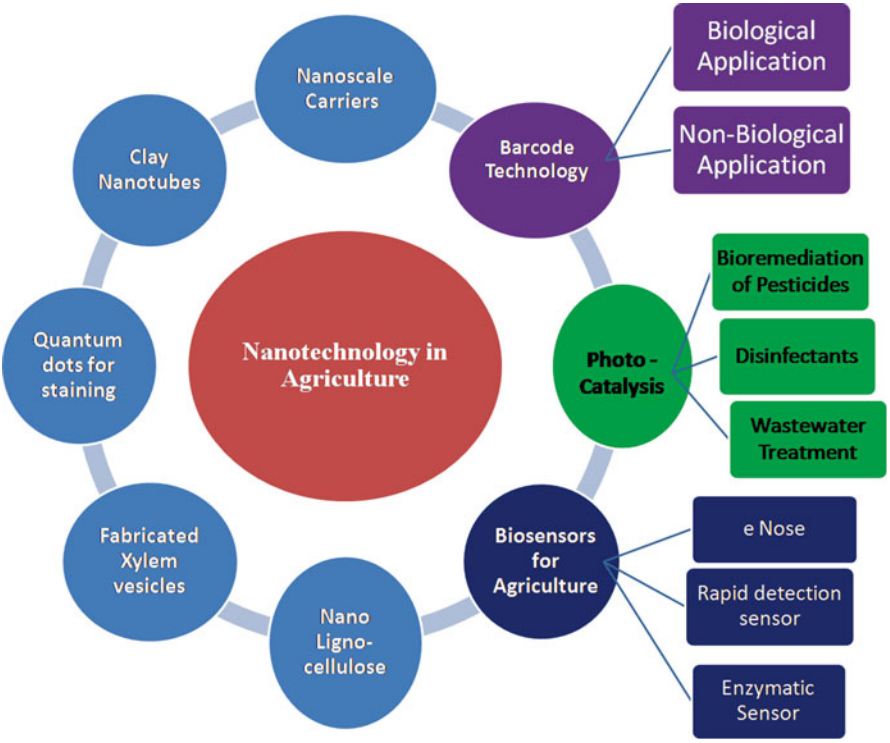


Fig. 1.5 Schematic representation for the application of nanotechnology in modern agriculture (Courtesy: Dasgupta et al. 2014)

matter in soil (Johnston 2010). These advances will help in increasing the bioavailability of active ingredients, thereby reducing the amount of inputs to be used and also the waste produced. Cai et al. (2014) developed nanoclays which can be added to traditional fertilizer to improve the retention capacity of nitrogen. Thus, nitrogen loss is reduced and sufficient nutrition is provided to crops. Many nanoemulsions have also been formulated to increase the bioavailability of herbicide and pesticide (Chaw et al. 2012, 2013; Megha et al. 2014).

1.3.2 Fabricated Xylem Vessels

Recent advancement in nanofabrication and characterization tools has enabled the study of physico-chemical and biological interactions of plant cell bodies and various disease-causing organisms. These tools are useful in understanding the mechanisms of pathogenesis and ultimately improved the strategies for the treatment of these diseases (Cursino et al. 2009; Chen and Yada 2011). To study xylem-inhabiting bacteria, changes in bacterial populations were monitored through destructive sampling techniques at different distances from inoculation sites but this does not provide information about colonization, film development, and subsequent movement and re-colonization at new areas because the same sample site cannot be followed temporarily. It has only been through the discovery of micro-fabricated xylem vessels with nano-sized features that we are able to study the above mechanisms which otherwise was not possible through traditional methods (Zaini et al. 2009; Allah 2012). A probe is used which can be inserted into the xylem vessel at the root base which can monitor xylem pressure, the radial electrical gradients in the root and activity of particular ions (Wegner 2012). A detailed description of nanotechnology in fabricated xylem vessels have been described by Bandyopadhyay et al. (2013) and fabricated xylem system in the form of nanoliter/picoliter scale fluidic systems have been summarized (Morgan et al. 2013). Biomimicking of micro/nanofabricated xylem vessels system by using microbes e.g. researchers have looked at the attachment behaviour of *Xylella fastidiosa* (Leonardo et al. 2007) and *Escherichia coli* (Bunpot et al. 2011) in microfluidic flow chambers mimicking plant xylem. Biomimicking of capillary action has been developed by using micro/nanofabrication – which may have future application in fabricated xylem vessel development (Qian et al. 2014; Bharat 2011). To control the photoluminescent emission Carlos et al. (2013) have used ZnO and Al_2O_3 nanoparticles in *Calamus rotang* plant *in natura* xylem samples.

1.3.3 Nanolignocellulosic Materials

Recently, nanosized lignocellulosic materials have been obtained from crops and trees which had opened a new market for innovative and value-added nano-sized materials and products, e.g. nano-sized cellulosic crystals have been used as lightweight reinforcement in polymeric matrix (Laborie 2009). These can be applied in food and other packaging, construction, and transportation vehicle body structures. Cellulosic nano-whisker production technology from wheat straw has been developed by Michigan Biotechnology Incorporate (MBI) International, and is expected to make biocomposites that could substitute for fibre glass and plastics in many applications, including automotive parts. North Dakota State University (NDSU) is currently engaged in a project for the commercialization of this technology (Leistritz et al. 2007). With the applications of food and other packaging, construction, and transportation vehicle body structures production of nanolignocellulosic materials is the best way for agricultural waste management – since we can derive nanolignocellulosic materials from lignin and cellulose based agricultural waste (Brinchia et al. 2013; Ming-xiong et al. 2014).

1.3.4 Clay Nanotubes

Clay nanotubes (Halloysite) have been developed as carriers of pesticides for low cost, extended release and better contact with plants, and they will reduce the amount of pesticides by 70–80 %, hence reducing the cost of pesticide and also the impact on water streams (Murphy 2008). The sorptive and electrical behaviour of nanocomposites (polylactide and carbon nanotubes/smectite-clay nanocomposites) was studied and found that polylactide nanocomposites are endowed with increased sorption and outstandingly enhanced conductivity (up to six or even nine orders of magnitude) with respect to the pristine polymer (Conductivity = $1 * 10^{-10}$ S/m) (Saveria et al. 2011). This increased sorptive and increased conductivity properties of nanocomposites may have the future application as selective purification of water and also this property can be applicable in plant-soil-water interface to increase the ion transport and sorption of nutrients. Hsu and Jheng (2009) have synthesized and characterized carbon nanotubes on clay minerals with the application of biosensor for glucose and hydrogen peroxide detection (Hsu and Jheng 2009) – which may has major applications in pre as well as post harvested agricultural products and their quality control. Suprakas (2013) has highlighted the tensile strength of clay/carbon nanotubes which may further be used in agricultural fields to provide strength to the crops and protect them from strong wind.

1.3.5 Photocatalysis

One of the processes using nanoparticles is photocatalysis. It involves the reaction of catalyst with chemical compounds in the presence of light. The mechanism of this reaction is that when nanoparticles of specific compounds are subjected to UV light, the electrons in the outermost shell (valence electrons) are excited resulting in the formation of electron hole pairs, i.e. negative electrons and positive holes (Zhaoxia et al. 2011). These are excellent oxidizing agents and include metal oxides like TiO_2 (Bhatkande et al. 2001; Khataee et al. 2013), Silver (Zhaoxia et al. 2011), gold (Vongani et al. 2011) ZnO (Li and Haneda 2003; Mohammad et al. 2011), SnO_2 (Ko et al. 2009), platinum (Zhi and Wenfeng 2014), Ag-α-Fe_2O_3 nanocomposites (Shaofeng et al. 2014), lanthanum ferrite Nanoparticles (Abazari et al. 2014), etc., as well as sulfides like ZnS (Feigl et al. 2010) and CdS (Xingyuan et al. 2014). As the size of particles decrease, surface atoms are increased, which results in tremendous increase in chemical reactivity and other physico-chemical properties related to some specific conditions such as photocatalysis, photoluminescence, etc. So this process can be used for the decomposition of many toxic compounds such as pesticides, which take a long time to degrade under normal conditions (Malato et al. 2002), e.g. pathogens. Ankita and Vidya (2014) have remediated reactive blue 220 dye with solar light induced photocatalytic degradation by using Ag core–TiO_2 shell (Ag@TiO_2) nanoparticles. They found higher rate of photocatalysis under solar light as compared to UV light and also Ag@TiO_2 is a better photocatalyst than Degussa-P25, TiO_2NP and Ag doped TiO_2 nanoparticle. It can be noted that Degussa-P25 is a existing product with these properties manufactured by Evonik Degussa India Pvt. Ltd. Their basic research may turn up with a development of WQM instruments and/or other agricultural engineering devices (Ankita and Vidya 2014). Using nano-titania Pigeot-Rémy et al. (2011) have used TiO_2 nanoparticle for photocatalysis and disinfection of water and also to decrease target bacterial load and a rectangular photoreactor has been designed and optimized (Fathinia and Khataee 2013). Recent research trend is shifting towards finding doped-nanoparticles with better efficiency for photocatalysis (Saraschandra et al. 2015; Tahir and Amin 2015; Sankar and Vijayanand 2015; Khataee et al. 2015).

1.3.6 Nanobioremediation

Nanoparticles can be used for the bioremediation of resistant or slowly degradable compounds like pesticides. These harmful compounds tend to join the positive holes, are degraded and converted into non-toxic compounds. Otherwise these harmful compounds enter the food chain and result in serious problems for the body, hence nanoparticles can be used for environmental safety (Lhomme et al. 2008). The main applications of nanotechnology in bioremediation (nanobioremediation) are as uranium remediation, hydrocarbon remediation, groundwater and wastewater remediation, solid waste remediation, heavy metal remediation. Some main nanomaterials involved in nanobioremediation are as: nanoiron and its derivatives, nano-sized dendrimers, carbon nanotubes, single enzyme nanoparticles, engineered nanoparticles etc. (Rizwan et al. 2014; Avinash et al. 2014). Engineered polymeric nanoparticles have been used in bioremediation of hydrophobic contaminants (Tungittiplakorn et al. 2005) and soil remediation (Tungittiplakorn et al. 2004). Biogenic uranite nanoparticles have been used for uranium bioremediation (Bargar et al. 2008). Biologically synthesized nanomaterials from organisms *Gundelia tournefortii*, *Centaurea virgata*,*Reseda lutea*, *Scariola orientalis*, *Eleagnum angustifolia*, *Bacillus* sp. and*Noaea Mucronata* accumulated heavy metals – mainly Cu, Zn, Pb, and Ni (Arvind et al. 2011; Avinash et al. 2014; Rizwan et al. 2014).

1.3.7 Disinfectants

The electron hole pair, especially the negative electrons resulting from the excitation of nanoparticles, can also be used as a disinfectant of bacteria, as when bacteria make contact with nanoparticles, the excited electrons are injected into their bodies, which results in the bacterial removal from the object concerned, as in fruit packaging and food engineering (Melemeni et al. 2009). Comparatively nanoparticles are better disinfectants than chemical disinfectants e.g. sodium hypochlorite (NaClO) and phenol (C_6H_5OH) etc. (Karthik et al. 2011).Wei et al. (2012) have concluded that the porous Ca-Si based nanospheres may be developed into a new intra-canal disinfectant-carrier for infected canal treatment. Nano-disinfectant in the form of biofilm has shown improved antimicrobial activity for *salmonella* and *staphylococcus* Sp. (Carla et al. 2012; Hans et al. 2012; Kumar and Ting 2013; Nithila et al. 2014).

1.3.8 Wastewater Treatment

In modern environmental science, the removal of wastewater is an emerging issue due to its effects on living organisms (Babula et al. 2008; Mulligan et al. 2001). Many strategies have been applied for wastewater treatment including nanotechnology. Photocatalysis can be used for purification, decontamination and deodorization of air. It has been found that semiconductor sensitized photosynthetic and photocatalytic processes can be used for the removal of organics, destruction of cancer cells, bacteria and viruses. Application of photocatalytic degradation has gained popularity in the area of wastewater treatment (Melemeni et al. 2009). The detailed mechanism of action (Fig. 1.6) for bactericidal/antimicrobial activity of nanomaterials has been described (Fahim et al. 2014). There will be differences

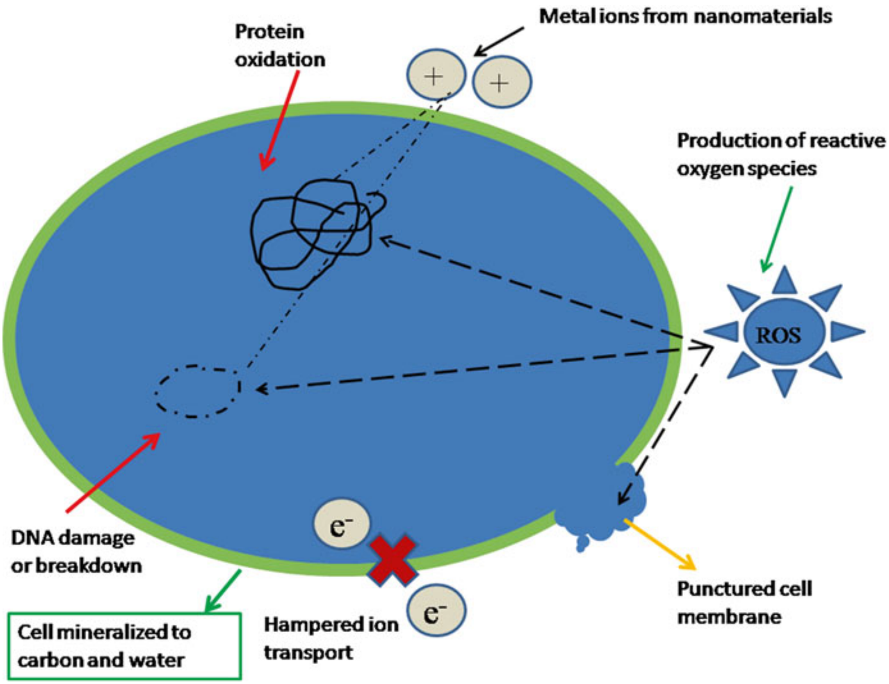


Fig. 1.6 Mechanism of bacteria cell damage by the induction of reactive oxygen species

between the mechanism of action for bactericidal activity of metal and metal oxide Nanoparticles (Solmaz et al. 2014). Understanding the differences in inactivation mechanisms helps to identify rate-limiting steps involved in the inactivation process as well as to develop more effective disinfection strategies. Detailed discussion on wastewater treatment is given in later section of this article.

1.3.9 Nanobarcode Technology

In our daily life, identification tags have been applied in wholesale agriculture and livestock products. Due to their small size, nanoparticles have been applied in many fields ranging from advanced biotechnology to agricultural encoding. Nanobarcodes (>1 million) have been applied in multiplexed bioassays and general encoding because of their possibility of formation of a large number of combinations that make them attractive for this purpose. The UV lamp and optical microscope are used for the identification of micrometer-sized glass barcodes which are formed by doping with rare earth containing a specific type of pattern of different fluorescent materials. The particles to be utilized in nanobarcodes should be easily encodeable, machine-readable, durable, sub-micronsized taggant particles. For the manufacture of these nanobarcode particles, the process is semi-automated and highly scalable, involving the electroplating of inert metals (gold, silver) into templates defining particle diameter, and then the resulting striped nanorods from the templates are released. These nanobarcodes have the biological as well as non-biological applications (Mathew et al. 2009). Cost effective nanobarcode technology development is a major challenge for the researchers – this can be concluded based on the fact that total of 18 documents found on Scopus indexed article database (SIAD). Out of 18 articles notes (1 in number), conference paper (6 in number) review article (2 in number) and only 9 research articles were available in last 10 years by the keyword of “nanobarcode” (SIAD 2014). Similarly, only 32 articles are present in SciFinder® database with the same keyword. After refining it with year wise none of the article were found for 2014; only one article in duplicate were found of Han et al. (2013) which have been discussed earlier; similarly, only three articles have been found for the year 2012 but none of them have described the application of nanobarcode in agricultural field (SciFinder 2014). This shows that development of nanobarcode technology for agricultural application is one of the thrust areas.

1.3.9.1 Biological Applications of Nanobarcodes

Nanobarcodes have been used as ID tags for multiplexed analysis of gene expression and intracellular histopathology. Improvement in the plant resistance against various environmental stresses such as drought, salinity, diseases and others have only been possible through advancement in the field of biotechnology at the nanoscale. In the near future, more effective identification and utilization of plant gene trait resources is expected to introduce rapid and cost effective capability through advances in nanotechnology-based gene sequencing (Branton et al. 2008). Nanobarcodes can also be used for cost- effective detection of pathogens from food products (Han et al. 2013).

1.3.9.2 Non-Biological Applications of Nanobarcodes

Nanobarcodes serve as uniquely identifiable nanoscale tags and have been applied for non-biological applications such as for authentication or tracking in agricultural food and husbandry products. This nanobarcode technology will enable us to develop new auto-ID technologies for the tagging of items previously not practical to tag with conventional barcodes (Branton et al. 2008).

1.3.9.3 Quantum Dots for Staining Bacteria

There are numerous bacteria which are responsible for many diseases in humans like tetanus, typhoid fever, diphtheria, syphilis, cholera, food-borne illness, leprosy and tuberculosis caused by different species. As a remedial process, we need to detect bacteria and for this, dye staining method is used. To stain bacteria, the most commonly used biolabels are organic dyes, but these are expensive and their fluorescence degrades with time. So the need of the hour is to find durable and economical alternatives. Fluorescent labelling by quantum dots with bio-recognition molecules has been discovered through the recent developments in the field of luminescent nanocrystals. Quantum dots are better than conventional organic fluorophores (dyes) due to their more efficient luminescence compared to the organic dyes, narrow emission spectra, excellent photostability, symmetry and tunability according to the particle sizes and material composition. By a single excitation light source, they can be excited to all colors of the Quantum dots due to their broad absorption spectra (Warad et al. 2004). Bio-labeled bacillus bacteria with Nanoparticles consisting of ZnS and Mn^{2+} capped with bio compatible ‘chitosan’ gave an orange glow when viewed under a fluorescence microscope. For the detection of *E. coli* O157:H7, Quantum dots were used as a fluorescence marker coupled with immune magnetic separation (Su and Li 2004). For this purpose, magnetic beads were coated with anti-*E. Coli* O157 antibodies to selectively attach target bacteria, and biotin-conjugated anti – *E. coli* antibodies to form sandwich immune complexes. Quantum dots were labelled with the immune complexes via biotin streptavidin conjugation after magnetic separation.

1.3.10 Biosensors

A variety of characteristic volatile compounds are produced by microorganisms that are useful as well as harmful to human beings, e.g. fermentation makes use of yeasts while alcohol is produced as a by-product when bacteria eat sugar. The most common causal organisms of food rotting are bacteria. Foul odour is a clear indication of food degradation which may be detected by visual and nasal sensation, but sometimes it may be impractical and a further cause for poisoning. Therefore, it is more sensible to use an instrument like rapid detection biosensors for the detection of these odours (Compagnone et al. 1995). The future application of nano-biosensors recently developed by Xiqi et al. (2014) and Zhang et al. (2014). Nanobiosensors are hot area of interest in the fields other than food and agriculture but recently many sensors have been developed after considering its importance. A detailed review on this has been done by Teresa (2013). ZigBee™ is a wireless mesh networking standard with low-cost and utilizes low-power. It has given the concept of 'Smart Fields' and 'SoilNet'. It consists of one or more sensors for environmental data (temperature, humidity, etc.), a signal conditioning block, a microprocessor/microcontroller with an external memory chip and a radio module for wireless communication between the sensor nodes and/or a base station. It can be used for the identification and monitoring of pests, drought or increased moisture levels in order to counterbalance their adverse effects on crop production (Kalra et al. 2010). Through this wireless sensor technology with nanoscale sensitivity, we can control plant viruses and level of soil nutrients, as the plant surfaces can be changed at nanoscale with specific proteins. This technology is important in realizing the vision of smart fields in particular. Wireless network sensor technology can also be used for monitoring the optimal conditions for mobile plants biotechnology.

1.3.10.1 Rapid Detection Biosensors

These instruments are able to reduce the time required for lengthy microbial testing and immunoassays. Applications of these instruments include detection of contaminants in different bodies such as water supplies, raw food materials and food products (Compagnone et al. 1995). Recently, nano biosensors are developed for rapid detection of IgG and metabolites (Labroo and Cui 2014; Türkoğlu et al. 2013).

1.3.10.2 Enzymatic Biosensors

Enzymes can act as a sensing element as these are very specific in attachment to certain biomolecules. According to Patel (2002), enzymatic biosensors on the basis of immobilization surface are classified into four groups (i) controlled-pore glass beads with optical transducer element, (ii) polyurethane foam with photo-thermal transducer element, (iii) ion-selective membrane with either potentiometric or amperometric transducer element and (iv) screen-printed electrode with amperometric transducer element. Considering microbial contamination a device (Electrogenerated chemiluminescence immunosensor) has been found by using Fe3O4@Au to detect *Bacillus thuringiensis* (Jianping et al. 2013). By keeping food and agricultural safety into consideration a biosensor using chemiluminescence and electro-chemiluminescence immunoassay have been found to detect botulinum neurotoxin serotypes A and B (Cheng and Stanker 2013). While considering aquaculture – to measure volatile amines levels in fishan optical fiber-based micro-analyzer was designed – this has future aspect as to develop such nano-biosensor instead of micro (Silva et al. 2010).

1.3.11 Electronic Nose

It is a device based on the operation of the human nose and is used to identify different types of odours; it uses a pattern of response across an array of gas sensors. It can identify the odorant, estimate the concentration of the odorant and find characteristic properties of the odour in the same way as might be perceived by the human nose. It mainly consists of gas sensors which are composed of nanoparticles e.g. ZnO nanowires (Hossain et al. 2005; Sugunan et al. 2005). ZnO nanorods are used to develop electronic nose which can detect impurities from vapour mixture (Ko et al. 2013). Their resistance changes with the passage of a certain gas and generates a change in electrical signal that forms the fingerprint pattern for gas detection. This pattern is used to determine the type, quality and quantity of the odour being detected. There is also an improved surface area which helps in better absorption of the gas.

1.3.12 Gold Nanoparticles

Gold nanoparticles, commercially used as rapid testing arrays for pregnancy tests and biomolecule detectors, are based on the fact that the colour of these colloids depends on the particle size, shape, refractive index of the surrounding media and separation between the nanoparticles. A quantifiable shift in the surface plasmon response (SPR) absorption peak results due to a small change in any of these parameters. We can make these nanoparticles attach to specific molecules by carefully choosing the capping agent for stabilizing gold nanoparticles. These specific molecules get adsorbed on the surface of these nanoparticles and change the effective refractive index of the immediate surroundings of the nanoparticles (Nath and Chilkoti 2004; Yuanyuang et al. 2010). A few nanoparticles will be adsorbed if the detecting molecules (bio-macromolecules) are larger than the gold nanoparticles and result in the formation of lumps after agglomeration. Ultimately, colour of gold nanoparticles is changed due to shift in SPR that result from the reduction of particle spacing. These properties provide a great opportunity to use gold nanoparticles for biosensor development. In the field of pharmaceutical science and other biomedical fields many Gold-nanoparticles-based biosensors have been already developed for detection of enzyme activity – the same should be researched in the field of food, agriculture and water quality management (Eliza and Dusica 2013).

1.4 Nanotechnology and Research Trends in Water Quality Management

Currently, provision of clean and abundant fresh water is one of the most important challenges faced by the world for human use and industrial applications such as agriculture (Vörösmarty et al. 2010; Allah 2012). According to a survey, more than one billion people in the world are deprived of clean water and the situation is getting worse. In the near future, it has been estimated that average water supply per person will drop by a factor of one third, which will result in the avoidable premature death of millions of people. Meanwhile non contaminated water is also not available for proper agricultural practices (Cross et al. 2009). A large amount of fresh water is required in agriculture, but in turn, it contributes to groundwater pollution through the use of pesticides, fertilizers and other agricultural chemicals. To combat this problem, novel, sustainable and cost effective technologies will be required for the treatment of this large amount of waste water produced. During the treatment of wastewater, critical issues like water quality and quantity, treatment and reuse, safety due to chemical and biological hazards, monitoring and sensors should be considered (Schoumans et al. 2014; Thorburn et al. 2013). Research and development in nanotechnology has enabled us to find novel and economically feasible solutions for remediation and purification of this wastewater. Accessible water resources are mostly contaminated with water-borne pathogenic microorganisms like cryptosporidium, coliform bacteria, virus, etc., various salts and metals (Cu, Pb, As), runoff agricultural chemicals, tens of thousands of compounds considered as pharmaceuticals and personal care products (PPCP), and endocrine disrupting compounds (EDC) and radioactive contaminants, either naturally occurring or as the result of oil and gas production as well as mining activities due to natural leaching and anthropogenic activities (Speed et al. 1987; Jasra et al. 1999). Nano-scale zerovalent iron can be used for the treatment of distillery wastewater (Homhoul et al. 2011). For improving water quality, nanotechnology has provided novel solutions (Fig. 1.7).

1.4.1 Nano-oligodynamic Metallic Particles

Physico-chemical microbial disinfection systems like chlorine dioxide, ozone and ultraviolet are being commonly used in developed countries, but most of the developing countries are lacking these systems due to the requirement of large infrastructure which make them costly. The need of the hour is to search and develop alternative cost-effective technologies. Nanotechnology based oligodynamic metallic particles have the ability to serve this function. Among these nanomaterials, silver is the most promising one as it is both bactericidal and viricidal due to the production of reactive oxygen species that cleaves DNA and can be utilized for a wide range of applications. Other properties include low toxicity, ease of use, its charge

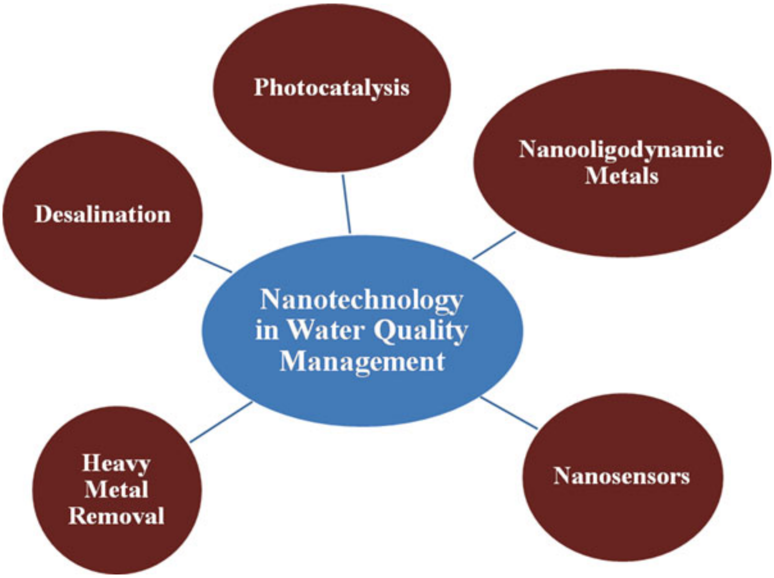


Fig. 1.7 Diagrammatic representation of nanotechnological aspects in water quality management which includes heavy metal removal, desalination, photocatalysis, nnao-oligodynamic metals and nano-sensors

capacity, high surface-to-volume ratios, crystallographic structure and adaptability to various substrates (Nangmenyi and Economy 2009; Chen and Yada 2011; Faunce et al. 2014; Jain et al. 2016). Recently researches have been done to vary the size of silver and gold nanoparticles with simple approaches i.e. changing the concentration of reactants. The improved activity of antimicrobial and anticancerous activity was observed for them (Nandita et al. 2015a; Maddineni et al. 2015; Shivendu et al. 2016; Janardan et al. 2016). It also can be noted that, recently trends are changing toward in silico and computational approach towards toxicity evaluation of inorganic nanoparticles (Ranjan et al. 2015, 2016).

1.4.2 Photocatalysis

Visible light photocatalysis of transition metal oxides, another nanoscale technological development, produces nanoparticles, nanoporous fibers and nanoporous foams that can be used for microbial disinfection (Li et al. 2009) and for the removal of organic contaminants like personal care products (PPCP) and endocrine disrupting compounds (EDC). Moreover, tubular nanostructures, embedded into microbial cell wall, can disrupt its cell structure resulting in the leakage of intracellular compounds, and ultimately cell death. A detailed research trends in the field of photocatalysis has been discussed above in detail. As discussed above – the recent research trends for photocatalysis using nanomaterials has been shifted from single nanoparticles to hybrid nanocomposite e.g. Ag/AgVO_3 one-dimensional hybrid nanoribbons with enhanced performance of plasmonic visible-light photocatalysis (Zhao et al. 2015); fabrication of plasmonic Pt nanoparticles on Ga-doped ZnO nanopagodas array with enhanced photocatalytic activity (Hsien-Ming et al. 2015); PbS quantum dots in ZnO@PbS/graphene oxide has been synthesized for enhanced photocatalytic activity (Xi-Feng et al. 2015); Zirconium and silver co-doped TiO_2 nanoparticles for degradation of methyl orange and methylene blue (Saraschandra et al. 2015).

1.4.3 Desalination

Due to limited resources of fresh water, it is likely that in the near future, desalination of sea water will become a major source of fresh water. Conventional desalination technologies like reverse osmosis (RO) membranes are being used but these are costly due to the large amount of energy required. Nanotechnology has played a very important role in developing a number of low-energy alternatives, among which three are most promising. (i) protein-polymer biomimetic membranes, (ii) aligned-carbon nanotube membranes and (iii) thin film nanocomposite membranes (Hoek and Ghosh 2009; Victor et al. 2014). These technologies have shown up to 1000 times better desalination efficiencies than RO, as these have high water permeability due to the presence of carbon nanotube membranes in their structure. Some of these membranes are involved in the integration of other processes like disinfection, deodorizing, de-fouling and self-cleaning. In another approach, zeolite nanomembrane can be used for seawater desalination (Liu and Chen 2013). Some of these technologies may be introduced in the market place in the near future but scale-up fabrication, practical desalination effectiveness and long-term stability are the most critical challenges to be considered before their successful commercialization (Yan et al. 2003). Desalination using nanotechnology with the aspects of carbon nanotubes (Rasel et al. 2014), reverse osmosis (Peng et al. 2011), forward osmosis for seawater and wastewater (Linares et al. 2014) have been reviewed earlier. Recently many devices with improved efficiency and performance have been developed- self-sustained webs of polyvinylidene fluoride electrospun nano-fibers (Essalhi and Khayet 2014); PVA/PVDF hollow fiber composite membrane modified with TiO_2 nanoparticles (Xipeng et al. 2014); novel integrated system coupled with nanofluid-based solar collector (Kabeel and Emad 2014); zinc oxide micro/nanostructures grafted on activated carbon cloth electrodes (Myint et al. 2014); tubular MFI zeolite membranes (Martin et al. 2012); titanium oxide nanotubes/polyethersulfone blend membrane (Abdallah et al. 2014); Graphene wrapped MnO2-nanostructures (Ahmed et al. 2014a); thin film nanocomposite membranes (Arun et al. 2014); Graphene/SnO2 nanocomposite (El-Deen et al. 2014; Ahmed et al. 2014b); carbon nanotubes (Goh et al. 2013).

1.4.4 Removal of Heavy Metals

Ligand based nanocoating can be utilized for effective removal of heavy metals as these have high absorption tendency. It becomes cost effective as it can be regenerated in situ by treatment with bifunctional self-assembling ligand of the previously used nanocoating media. Farmen (2009) used crystal clear technology for water purification in which multiple layers of metal can be bonded to the same substrate using crystal clear technologies (Farmen 2009). According to, another strategy for the removal of heavy metals is the use of dendrimer enhanced filtration and it can bind cations and anions according to acidity (Diallo 2009). Nowadays nanomaterials have been widely used to remove heavy metals from water/wastewater due to their large surface area and high reactivity. Metal oxide nanoparticles, including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, provide high surface area and specific affinity for heavy metal adsorption from aqueous systems. To date, it has become a hot topic to develop new technologies to synthesize metal oxide nanoparticles, to evaluate their removal of heavy metals under varying experimental conditions, to reveal the underlying mechanism responsible for metal removal based on modern analytical techniques (XAS, ATR-FT-IR, NMR, etc.) or mathematical models, and to develop metal oxide-based nanomaterials of better applicability for practical use i.e. granular oxides or composite materials (Ming et al. 2012). Additionally, humic acid and fulvic acid exist ubiquitously in aquatic environments and have a variety of functional groups which allow them to complex with metal ions and interact with nanomaterials. These interactions can not only alter the environmental behaviour of nanomaterials, but also influence the removal and transportation of heavy metals by nanomaterials. Thus, the interactions and the underlying mechanisms involved warrant specific investigations. Wang-Wang et al. (2014) have given a detailed review on the effects of humic acid and fulvic acid on the removal of heavy metals from aqueous solutions by various nanomaterials, mainly including carbon-based nanomaterials, iron-based nanomaterials and photocatalytic nanomaterials. Mainly they have discussed the mechanisms involved in the interactions and evaluated the potential environmental implications of humic acid and fulvic acid to nanomaterials and heavy metals.

1.4.5 Wireless Nanosensors

Crop growth and field conditions like moisture level, soil fertility, temperature, crop nutrient status, insects, plant diseases, weeds, etc. can be monitored through advancement in nanotechnology. This real-time monitoring is done by employing networks of wireless nanosensors across cultivated fields, providing essential data for agronomic intelligence processes like optimal time of planting and harvesting the crops. It is also helpful for monitoring the time and level of water, fertilizers, pesticides, herbicides and other treatments. These processes are needed to be administered given specific plant physiology, pathology and environmental conditions and ultimately reduce the resource inputs and maximize yield (Scott and Chen 2003). Scientists and engineers are working to develop the strategies which can increase the water use efficiency in agricultural productions, e.g. drip irrigation. This has moved precision agriculture to a much higher level of control in water usage, ultimately towards the conservation of water. More precise water delivery systems are likely to be developed in the near future. These factors critical for their development include water storage, in situ water holding capacity, water distribution near roots, water absorption efficiency of plants, encapsulated water released on demand, and interaction with field intelligence through distributed nano-sensor systems (Cross et al. 2009). Sensing and detection of various contaminants in water at nanoscale under laboratory and field conditions has remained a hot issue over the last decade. In the near future, state-of-the-art nanotechnology-based techniques will help in developing many new technologies that will have better detection and sensing ability (Chen and Yada 2011). Similar to nanobarcode development – wireless nanosensor development for WQM is one of the vital fields of the research. Sensor networks are a key technological and economic driver for global industries in the near future, with applications in health care, environmental monitoring, infrastructure monitoring, national security, and more. Developing technologies for self-powered nanosensors is vitally important. Zhong (2012) has given a brief summary about recent progress in the area, describing nanogenerators that are capable of providing sustainable self-sufficient micro/nanopower sources for future sensor networks. Negligible research work has been done in the field of wireless nanosensor development (SIAD 2014; SciFinder 2014) out of which mostly are conceptual notes and/or book chapters and reviews. Mannoor et al. (2013) have done an outstanding work after developing wireless raphene-based nanosensor for detection of bacteria. In particular, they have demonstrated integration onto a tooth for remote monitoring of respiration and bacteria detection in saliva. Since they have developed a wireless nanosensor to detect bacterial load in saliva which is an aqueous phase – by keeping this concept in mind one can think about developing such device for bacterial load detection.

It can be noted that other than food and agriculture, nanotechnology has grown interest in many fields. Figure 1.1 represents the allied fields and Fig. 1.8 represents the patents (Edgar et al. 2011). The beneficial properties – increased surface area, apparent solubility, good retention time, direct uptake of nanomaterials, and enhanced nutritional quality – open the ample scope for the nanotechnology with different applications and have best future to cover the market has been summarized in Fig. 1.9. On contrary, one should not ignore the toxicological aspect of nanomaterials on humans, animals and its impact on ecosystem, the same has been discussed in other chapters of this book (Fig. 1.10).

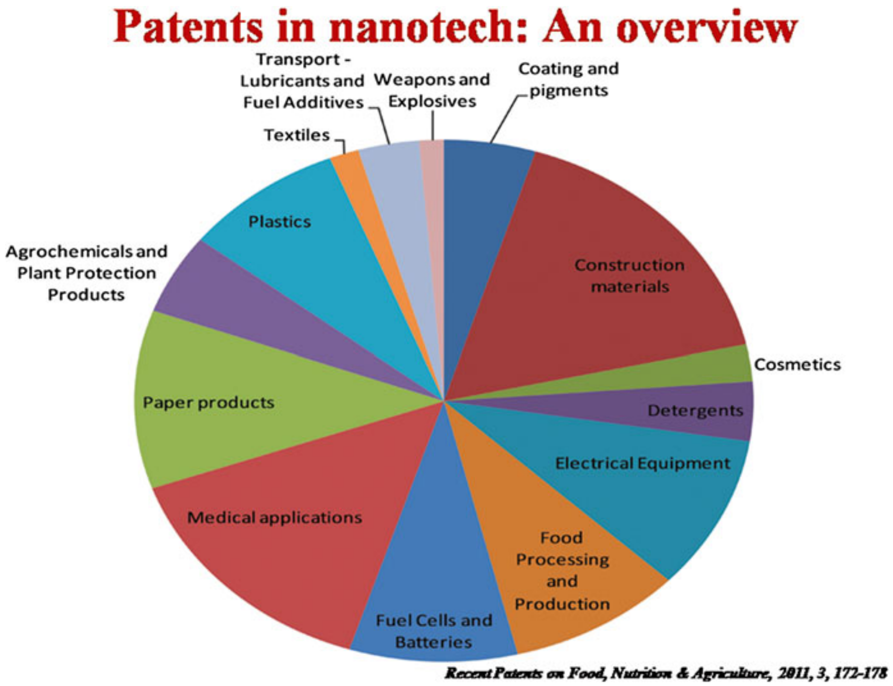


Fig. 1.8 A diagrammatic representation of patents in different applied nanotechnology sector in previous decade. It represents the sharp increase in use of nantechnology in different sectors including agriculture and foods (Courtesy: Edger et al. 2011)

1.5 Conclusion

Nanotechnology has not only improved the quality of modern agricultural practices by making them technical, susceptible, safer and improved quality in agricultural products nutritious but have also helped a lot in generating new agricultural products, better packaging and storage techniques and improved the quality of the its allied field such as water quality management. Conversion of materials to its nano form helps in enhancement of their physiochemical properties and applications e.g. silver nanoparticles shows antibacterial property and they are being incorporated into bandages for their beneficiary effect in ailing wound; however the bulk particles are less effective. Titanium dioxide, used as an intense white pigment is opaque in nature. However, nanoparticles of titanium dioxide are transparent and due to its physical nature, they are being used in transparent sunscreens, food packaging or plastic food containers.

Application of nanotechnology has enhanced the delivery of fertilizers, pesticides, herbicides and plant growth regulators with the help of nanoscale carriers; also its application in agricultural sector as fabricated xylem vessel, clay nanotubes,

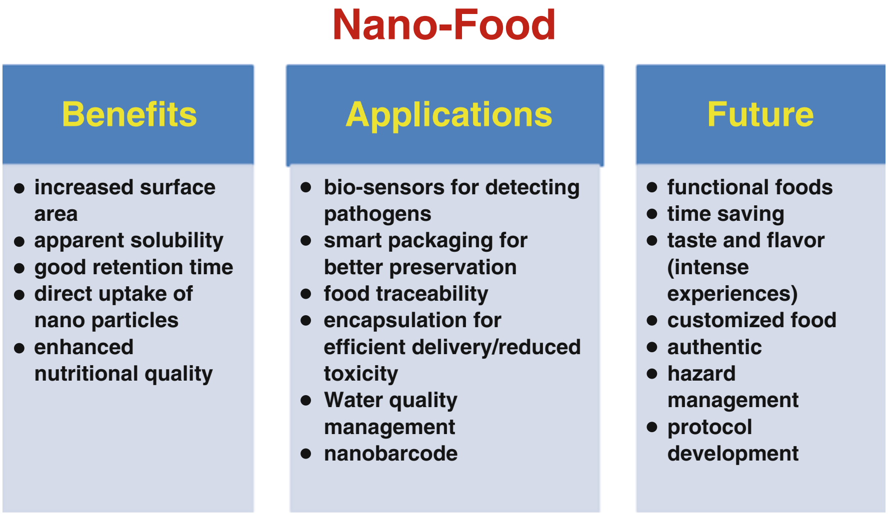


Fig. 1.9 The beneficial properties – increased surface area, apparent solubility, good retention time, direct uptake of nanomaterials, and enhanced nutritional quality – open the ample scope for the nanotechnology with different applications and have best future to cover the market

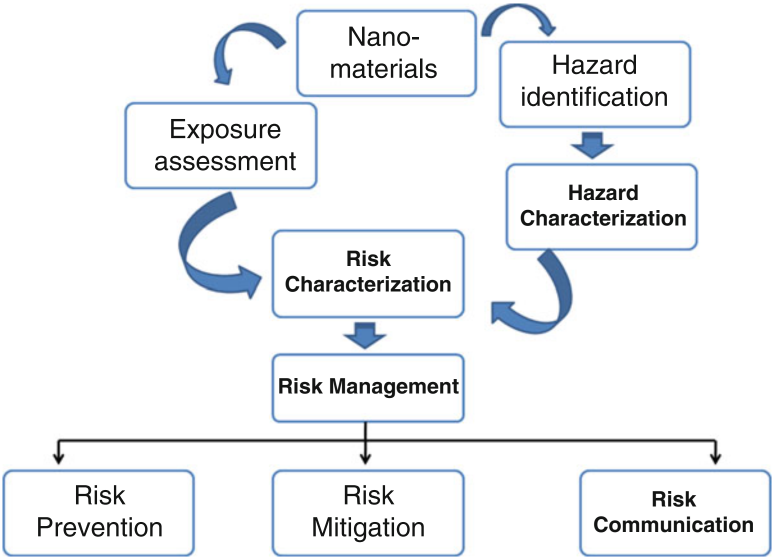


Fig. 1.10 The toxicological aspect of nanomaterials on humans, animals, environment and whole ecosystem. Diagrammatic representation of overview of nano-toxicological analysis

photocatalysis, wastewater treatment, nanobarcode technique, different types of biosensors, Quantum dots for bacterial staining etc. In addition, nanomaterials are further researched to keep the product fresher with increased shelf life. Nanoscience and nanotechnologies have vast applications in water quality managementas heavy metal removal, nano-bioremediation through nanolignodynamic metals, desalination, disinfecting process and the sensors to check the quality. Nevertheless, many of their applications are currently at a beginning stage and most of them require a high quality of research and development for their safe application. The safety of nanoparticles in agri-food industry also offers challenge to government and industry both. The food processing industry must ensure the consumer confidence and acceptance of nanofoods safety. When it comes to the application of nanotechnology in industrial scale, it is important to evaluate the release of nanoparticles into the environment and to estimate the subsequent levels of exposure to these materials. As the nanoparticles can easily penetrate into the human organ and organelles, exposure time, exposure concentrations, sites of penetration, immune response and accumulation and retention of nanoparticles in body and their subsequent effects should be assessed carefully.

Even though the research regarding the application of nanotechnology is growing every day, still insufficient scientific examination of naturally occurring nanosystems is available. The compulsory testing of nano-modified agricultural products and/or treated water should be performed before they allowed to be introduced into the market. Standardized test procedures are required to study the impact of nanoparticles on living cells for evaluation of the risk assessment on human exposure to nanoparticles. Toxicology of nanoparticles is poorly understood because of the lack of validated test methods and the inconsistency in the reported data. The inconsistency in the published data is due to the improper characterization of nanoparticles and the interferences induced by the nanoparticles in the available test system. Hence, the regulatory bodies and the policy makers should provide the guidance document for the validated protocols, safe uses and the disposal of the nanoparticles. The understanding of the safe application of nanoscience and nanotechnology in agri-food and water quality management will help in the sustainable growth of “nanoagri-technology”.

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Chapter 2
Nanotechnology Definitions, Research, Industry and Property Rights

Namita Ashish Singh

Abstract Nanotechnology uses nanomaterials for human benefit. In this chapter I present the various nanomaterials such as liposomes, nanowires and carbon nanotubes. The next section describe nanotechnology research in biomedial, food, agriculture and environmental sciences. Then I present nanotechnology application in the oil, textile, food and cosmetic industry. Intellectual property rights are discussed in the last section.

Keywords Nanotechnology • Biomedical • Agri food • Textile • Oil and gas industry • Cosmaceuticals • Patents

2.1 Introduction

Nanoscale refers size dimensions between approximately 1–100 nm (or more appropriately, 0.2–100 nm) because at this scale the properties of materials differ with respect to their physical, chemical and biological properties from a larger scale. Any form of a material that has one or more dimensions in the nanoscale is known as nanomaterial (Sekhon 2014). Nanoparticles have unique biological properties like small size, large surface area-to-volume ratio which allows them to bind, absorb and carry compounds such as small molecule drugs, DNA, RNA, proteins, and probes with high efficiency (Khan et al. 2015; Nandita et al. 2016b).

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2.1.1 Nanoparticles Types

2.1.1.1 Liposomes

Liposomes are the simplest forms of nanovectors (hollow or solid structured nanoparticles which can be filled with various anticancer drugs, targeting moieties and detection agents) which are made up of lipids enclosing water core (Park 2002).

2.1.1.2 Dendrimers

Dendrimers are artificial macromolecules having tree like structures in which atoms are arranged in many branches radiate from a central core. Dendrimers are self assembling synthetic polymers which were used in the magnetic resonance imaging of lymphatic drainage in mouse model of breast cancer (Kobayashi et al. 2004).

2.1.1.3 Nanoshells

Nanoshells are other nanoparticles composed of a gold shell surrounding a semiconductor.

2.1.1.4 Nanowires

Nanowires are sensing wires coated with antibodies like molecules to bind to proteins of interest. Silicon nanowires are real time detectors for molecular binding effects.

2.1.1.5 Fullerenes Based Derivatives

Fullerenes are nanostructured arrangement of carbon atoms in specific soccer like architecture. They may also form nanotubes which are cylindrical carbon atom assemblies. Fullerenes have found several specific sensing applications.

2.1.1.6 Quantum Dots

Quantum Dots are inorganic fluorescent semiconductor nanoparticles composed of 10–50 atoms with a diameter ranging 2–10 nm (Cai and Chen 2007).

2.1.1.7 Gold Nanoparticles

Gold nanoparticles have been used in vitro based on their ability to scatter visible light (Sokolov et al. 2003).

2.1.1.8 Carbon Nanotube

Carbon nanotubes are cylinders of several graphite layers with a diameter in nanometers. They may be classified into single-walled carbon nanotubes and multiwalled carbon nanotubes. Due to their unique electronic, thermal and structural characteristics carbon nanotubes they offer a unique approach for drug and gene delivery (Tanaka et al. 2004).

2.1.1.9 Nanobiosensors

A device used for detection of an analyte through combination of a sensitive biological component, transducer along with a detector component is termed as a biosensor (Mody 2011).

Nanotechnology uses include nanoparticle-mediated gene or DNA transfer in plants for the development of insect-resistant varieties, food processing and storage; nano feed additives, and increased product shelf life. The agri-food theme focuses on sustainability and protection of agriculturally produced foods, including crops for human consumption and animal feeding. Nanotechnology provides new agrochemical agents and new delivery mechanisms to improve crop productivity. Nanotechnology can boost agricultural production, by nanoformulations of agrochemicals for applying pesticides and fertilizers for crop improvement. Nanosensors or nanobiosensors can be used in crop protection for the identification of diseases and residues of agrochemicals (Sekhon 2014).

Nanoliposome applications in medicine include molecular imaging, disease diagnosis, bioactive encapsulation and passive or active targeted delivery. Some of the current nanocarrier systems are nanoscale size of conventional systems, such as nanocrystals, micelles, nanoliposomes and dendrimers (Park 2007).

An ‘oil-microbe detection tool’, using nano optical fibers has been developed to detect the by passed oil or the oil left behind after water flooding (Jahagirdar 2008). Nanotechnology produces nanomaterials with many attractive properties, which can play an important role in reducing friction, eliminating differential pipe sticking, maintaining borehole stability, protecting reservoir, and enhancing oil and gas recovery. Nanomaterials also have potential for oil well drilling operations in the forms of nanoscale drilling fluid additives and nanofluids in petroleum development (Kasiralvalad 2014).

2.2 Research Innovations

2.2.1 Nanotechnology Biomedical Applications

Nanoparticles are used for disease diagnosis, drug delivery, gene therapy of cancer, pulmonary diseases and prevention of other infections also. Cancer is one of the leading causes of death worldwide. Cancer is malignant neoplasm, there is uncontrolled division of cells which enter into normal adjacent tissues and destroy them (Maddinedi et al. 2015). There are different nanoparticle based delivery systems are available for therapeutic and diagnostic uses as depicted in Table 2.1.

Liposomes are coated with polyoxyethylene which prevent opsonisation of liposomes and their uptake by macrophages (Senior et al. 1999). The drug is targeted to the target site passively owing to the physiological conditions of the body. Various Doxorubin encapsulated liposomal formulations have been clinically utilized for the treatment of Kaposi's sarcoma, breast cancer and ovarian cancer (Palao 2004). Cancer drugs like amphotericin and haymycin, when used as liposomal drugs produce much better efficacy and safety as compared to conventional preparations. Majoros et al. (2006) have shown the synthesis, characterization and functionality of Poly (Amidoamine) dendrimer based anticancer therapeutics.

When nanoshells they reach the cancer cells, they can be irradiated. These irradiations make them hot which ultimately kill the cancer cells. This technique has been successfully utilized in veneral tumours in mice (Hirsch et al. 2003). Nanowire based arrays are used for early diagnosis of cancer and cancer treatment. Quantum dots due to their long term, high sensitivity and multicontrast imaging properties they are used for detection and diagnosis of cancer in vivo (Morrow et al. 2007).

Sokolov et al. (2003) successfully used gold nanoparticles conjugated to antibodies to level cervical biopsies for identification of precancerous lesions. The use of nanobiosensors in cancer clinical testing have been increased due to high speed,

Table 2.1 Nanoparticle based delivery systems for therapeutic and diagnostic uses

Nanoparticle based delivery systems	Therapeutic and diagnostic use
Liposomes	Controlled and targeted drug delivery, targeted gene delivery
Dendrimers	Targeted drug delivery
Nanoshells	Tumour targeted
Nanowires, fullerenes based derivatives	As targeting and imaging agents
Quantum dots	As targeting and imaging agents
Gold nanoparticles	Targeted delivery and imaging agents
Carbon nanotube	Drug gene and DNA delivery, tumor targeting
Nanobiosensors	Early diagnosis of cancer and detection of cancer agents

reduced cost for diagnosis, automation and multi target analysis (Rasooly 2006; Wang 2006). Nanobiosensors are useful for early diagnosis of cancer. They can also effectively be utilized for the detection of cancer agents such as environmental pollutants, pathogens and carcinogenic gases (Mody 2011).

Nanocarriers can be applied for pulmonary therapies, they penetrate or overcome blood brain barrier, branching pathways of the pulmonary tract, and the tight epithelial junctions of the skin (Courrier et al. 2002; Hughes 2005). Nanosilver is also used as a biocide to prevent infection in burns, traumatic wounds, and diabetic ulcers (Silver et al. 2006).

Fullerene compounds can be employed as antiviral agents, most notably against human immuno-deficiency virus (Schinazi et al. 1993) antibacterial agents e.g., *Escherichia coli*, *Streptococcus*, *Mycobacterium tuberculosis* (Tsao et al. 1999a; b; Bosi et al. 2000). Fullerene compounds are also used as antioxidant and antiapoptotic agents for the treatment of amyotrophic lateral sclerosis (Dugan et al. 2000) and Parkinson's disease (Cai et al. 2008) and in many other applications.

Cochleates are small lipid-based carriers consist of a negatively charged lipid and a divalent cation. Cochleates and nanocochleates have been used to deliver peptides, proteins, DNA for vaccine and gene therapy. Due to their nanometric size, stability and resistance to degradation in the gastrointestinal tract, nanocochleates have revealed great potential to deliver bioactive agents both orally and parenterally. Cochleates containing amphotericin B are now in development for the oral and parenteral treatment of fungal infections (Mozafari 2006; Darani and Mozafari 2010).

2.2.2 Nanotechnology in Agri-Food Production

2.2.2.1 Nanotechnology for Crop Improvement

A variety of nanomaterials, mostly metal-based nanomaterials and carbon-based nanomaterials, have been exploited for their absorption, translocation, accumulation, and effects on growth and development of crop plants (Nair et al. 2010; Rico et al. 2011). The positive morphological effects included enhanced germination percentage and rate, length of root and shoot, their ratio and vegetative biomass of seedlings in many crop plants, including corn, wheat, ryegrass, alfalfa, soybean, rape, tomato, radish, lettuce, spinach, onion, pumpkin, cucumber etc. Enhancement of many physiological parameters such as enhanced photosynthetic activity and nitrogen metabolism by metal-based nanomaterials in a few crops including soybean (Agrawal and Rathore 2014; Nandita et al. 2015a). Magnetic nanoparticles coated with tetramethylammonium hydroxide led to an increase in chlorophyll-a level in maize.

Nanobiosensors can be effectively used for sensing a wide variety of fertilizers, herbicide, pesticide, insecticide, pathogens, moisture, soil pH, and their controlled use can support sustainable agriculture for enhancing crop productivity (Guo 2004).

2.2.2.2 Nanofoods

The agri-food industries have been investing huge money into nanotechnology research. Food is nanofood when nanoparticles or nanotechnology techniques or tools are used during cultivation, production, processing, or packaging of the food (Ranjan et al. 2014). Foods among the nanotechnology-created consumer products coming onto the market include a brand of canola cooking oil called Canola Active Oil (Shemen Industries, Tel Aviv, Israel), a tea called Nanotea (Qinhuangdao Taiji Ring Nano-Products Co., Ltd., Hebei, People's Republic of China), and a chocolate diet shake called Nanoceuticals Slim Shake Chocolate (RBC Life Sciences Inc., Irving, TX, USA). The canola oil contains an additive called "nanodrops" designed to carry vitamins, minerals, and phytochemicals through the digestive system and urea (Washington DC 2013).

2.2.3 Nanofertilizers

Traditional fertilizers substitution by nanofertilizers is a way to release nutrients into the soil gradually thus preventing autrification and pollution of water resources (Moaveni and Kheiri 2011; Naderi and Abedi 2011). Treatment with TiO_2 nanoparticles on maize had a considerable effect on growth, titanium nanoparticles increases light absorption and photo energy transmission. A compound of SiO_2 and TiO_2 nanoparticles increased the activity of nitrate reductase in soybeans and intensified plant absorption capacity, making its use of water and fertilizer more efficient (Lu et al. 2002; Ranjan et al. 2016).

Nanofertilizers have unique features like ultrahigh absorption, increase in production, rise in photosynthesis, and significant expansion in the leaves' surface area. The use of nanofertilizer leads to an increased efficiency of the elements, reduces the toxicity of the soil, to at least reach the negative effects caused by the consumption of excessive consumption of fertilizers, and reduces the frequency of application of fertilizers (Naderi and Danesh-Shahraki 2013).

2.2.4 Nanotechnological Applications in Agrowaste Reduction and Biofuels

Nanomaterials could stimulate microorganism metabolism. Nanomaterials could improve the efficiency of the lipid extraction and without harming the microalgae. Nanomaterials such as calcium oxide and magnesium oxide nanoparticles have been used as biocatalyst carriers in oil transesterification to biodiesel. The advances in application of nanotechnology in microalgae lipid accumulation extraction, and transesterification were reported (Zhang et al. 2013). Cellulose-based nanomaterials have been used as potential nanoreinforcing filler into biocomposites for industrial and biomedical applications (Kumar et al. 2014).

2.2.5 Nanoagrochemicals

Pesticides are commonly used in agriculture to improve crop yield and efficiency. Nanopesticides are new strategies used to address the problems of agriculture (Sasson et al. 2007). Nanomaterials serve equally as additives (mostly for controlled release) and active constituents (Gogos et al. 2012). Controlled-release formulations of imidacloprid, synthesized from polyethylene glycol and various aliphatic diacids using encapsulation techniques, have been used for efficient pest management in different crops. In addition, some of the developed controlled-release formulations recorded higher yield over commercial formulation and control (Adak et al. 2012). Researchers have reported different aspects of nanoparticle formulation, characterization, effect of their characteristics, and their applications in management of plant diseases (Al-Samarrai 2012).

2.2.6 Nanomaterials Based Biosensor for Bacterial Contaminants in Milk

An amperometric immunobiosensing strip with conjugating secondary enzyme-labeled antibodies with gold nanoparticles has been developed to detect to detect *Listeria monocytogenes* at two log colony-forming unit (CFU)/g in wild blueberry samples. This method showed significant specificity over other enteric pathogens such as *Escherichia coli O157:H7* and *Salmonella typhimurium* (Davis et al. 2013).

2.2.7 Nanotechnology in Oil Industry

Nanotubes have many potential applications within the oil industry. For instance, nanotubes could be used to create lighter, stronger, and more corrosion-resistant structural materials. Nanotechnology could help improve oil and gas production by making it easier to separate oil and gas in the reservoir for instance, through improved understanding of processes at the molecular level. There are many other potential clean energy sources that could be enhanced through the use of nanotechnology. One specialized petroleum laboratory has developed an advanced fluid mixed with nanosized particles and superfine powder that significantly improves the drilling speed and can eliminate formation damage in near wellbore zone (Abdollah 2009). Subsurface micro and nanosensors could be injected in oil and gas well bores for recovery (Kong and Ohadi 2010).

2.2.8 Nanotechnology in Gas Industry

Nanotechnology could be used to enhance the possibilities of developing unconventional gas resources. Near-term challenges focus on liquefied-natural-gas infrastructure, efficiency, quality and developing gas-to-liquids technology. Midterm challenges include developing superpipelines; constructing floating gas-to-liquids platforms; production, regasification, and storage issues; and compressed-natural-gas transport. Long-term issues are production of methane hydrates and gas by wire producing electricity at the location of the gas source and carrying the electricity by wire to market rather than the gas to market by pipeline. Nanotechnology can address the problems associated with accessing stranded natural-gas resources by developing nano catalysts and nanoscale membranes for gas-to-liquids production and creating nano structured materials for compressed-natural-gas transport or long-distance electricity transmission (Abdollah 2009).

The recovery of gas from hydrates requires the dissociation of gas hydrates, air-suspended Ni-Fe nanoparticles when injected in the hydrate formation they will penetrate deep into hydrate reservoir by passing through the cavities. The self-heating of Ni-Fe particles in a magnetic field is caused by hysteresis loss and relaxation losses. These particles cause a temperature rise up to 42 °C leading to disturbance in thermodynamic equilibrium and causing the water cage to decompose and release methane (Bhatia and Chacko 2011).

2.2.9 Nanotechnology in Textile Industry

Nanotechnology is applied in textile industry due to the increased durability of fabrics, comfortness, hygienic properties and reduced production cost. Nanotechnology also offers many advantages as compared to the conventional process in term of economy, energy saving, eco-friendliness, control release of substances, packaging, separating and storing materials on a microscopic scale for later use and release under control condition (David 2002).

Nanoparticles can provide high durability for treated fabrics as they posses large surface area and high surface energy that ensure better affinity for fabrics and led to an increase in durability of the desired textile function. The particle size also plays a primary role in determining their adhesion to the fibres. It is reasonable to accept that the largest particle cluster will be easily removed from the fibre surface, while the smallest particle will penetrate deeper and adhere strongly into the fabric matrix (Kathiervelu 2003; Wang and Chen 2005). Thus due to the decreasing size of particles to nano-scale dimensional, changes in the properties of the material occurs.

Table 2.2 Some finishing based developments through nanotechnology in textile industries

Application in textile	Nanomaterials used	References
Electro conductive and antistatic	Carbon black, carbon nanotubes (CNT), Cu, Polypyrrole, Polyaniline	Dong and Huang (2002) and Anonymous (2003)
Increase durability	Al_2O_3, SiO_2, CNT, ZnO, Polybutylacrylate	Burniston et al. (2004) and Wong et al. (2006)
Antibacterial	Ag, Chitosan, SiO_2 (as matrix),TiO_2 , ZnO	Burniston et al. (2004), Wong et al. (2006) and Nandita et al. 2015b
Self-cleaning/dirt and water repellent	CNT, Fluoroacrylate, SiO_2 (as matrix), TiO_2	Lei and Juan (2003) and Zhang et al (2003)
Moisture absorbing	TiO_2	Burniston et al. (2004)
UV protection	TiO_2, ZnO	Burniston et al. (2004) and Wong et al. (2006)
Controlled release of active agents, medicinal products or fragrances	Montmorillonite (nano clay), SiO_2 (as matrix)	Harholdt (2003)

Areas where nanotech enhanced textiles are already seeing some applications include sporting industry, skincare, space technology and clothing as well as materials technology for better protection in extreme environments.

The use of nanotechnology allows textiles to become multifunctional and produce fabrics with special functions, including antibacterial, UV-protection, easy-clean, water and stain repellent and anti-odour: Kathiervelu (2003) as shown in Table 2.2.

To impart wrinkle resistance to fabric, resin is commonly used in conventional methods. However, there are limitations to applying resin, including a decrease in the tensile strength of fibre, abrasion resistance, water absorbency and dye-ability, as well as breathability. To overcome the limitations of using resin, some researchers employed nano-titanium dioxide and nano-silica to improve the wrinkle resistance of cotton and silk. Nano-titanium dioxide is used with carboxylic acid as a catalyst under UV irradiation to catalyse the cross-linking reaction between the cellulose molecule and the acid while nano-silica is used with maleic anhydride as a catalyst to improve the wrinkle resistance (Song et al. 2001; Zhou et al. 2003; respectively (Wong et al. 2006).

Silver nanoparticles are used in socks and sports clothing because of their ability to kill bacteria and inhibit unwanted odors (Medero 2013).

2.2.10 Nanotechnology in Food Industry

Nanoscience applications in foods suggested the technologies that create added values that are most needed and that will have the highest impact on consumers. Four major types of applications of nanotechnology in the food industry namely agriculture, food processing, food packaging, and supplements are described in Table 2.3.

Table 2.3 Application of nanotechnology being researched, tested, and applied in the food industry

Agriculture	Food processing	Food packaging	Supplements
Nanotechnology enabled single molecule detection for determining enzyme/substrate interactions	Nanocapsules for improving bio-availability of neutraceuticals in standard ingredients such as cooking oils	Fluorescent nanoparticles with attached antibodies for detecting chemicals or food-borne pathogens	Nanosize powders for increasing absorption of nutrients
Nanopsules for delivery of pesticides, fertilizers, and other agri-chemicals	Nano encapsulated flavor enhancers	Biodegradable nanosensors for temperature, moisture, and time monitoring	Cellulose nanocrystal composites as drug carriers
Nanotechnology enabled delivery of growth hormones in a controlled fashion	Nanotubes and nanoparticles as gela-tion and viscosifying agents	Nanoclays and nanofilms as barrier materials to prevent spoilage and oxygen absorption	Nanocochleates (coiled nanoparticles) for more efficient nutrient delivery to cells without affecting color or taste of food
Nanosensors for monitoring soil conditions and crop growth	Nanocapsule infusions of plant-based steroids as a replacement for meat cholesterol	Electrochemical nanosensors for detecting ethylene	Vitamin sprays that disperse nanodroplets with better absorption
Nanochips for identity preservation and tracking	Nanoparticles that selectively bind and remove chemicals or pathogens from food	Nanoparticle containing anti-microbial and antifungal surface coatings	
Nanosensors for detecting animal and plant pathogens	Nanoemulsions and nanoparticles for better availability and dispersion of nutrients	Lighter, stronger, and more heat-resistant films made of silicate nanoparticles	

Pray and Yaktine (2009); Nandita et al. 2015a

Cow udder cell produces casein micelles and fat globules, both key ingredients of milk, with casein micelles ranging in size from 300 to 400 nm and fat globules ranging in size from 100 nm to 20 μm. Fat globule membranes have a thickness of 4–25 nm. The dairy industry utilizes these three basic micro and nano-sized structures to build all sorts of emulsions (butter), foams (ice cream and whipped cream), complex liquids (milk), plastic solids (cheese) and gel networks (yogurt) (See and Stanley 1999).

Nanocomposites focus on the development of high barrier properties against the diffusion of oxygen, carbon dioxide, flavor compounds, and water vapor. Bionanocomposites suitable for packaging applications include starch and cellulose derivatives, poly lactic acid, poly caprolactone, poly butylenes succinate and polyhydroxy-butyrate. Nanoclay (montmorillonite, a hydrated alumina silicate layered clay consisting of an octahedral sheet of aluminum hydroxide between two silica layers) minerals are found abundantly in nature and might be incorporated into the packaging films. The use of nanocomposites with new thermal and gas barrier properties can prolong the post-harvest life of food and this application could facilitate the transportation and storage of food.

Nanolaminates, which consist of two or more layers of nano-materials (physically or chemically bonded to each other), are suitable for use in the food industry. Nanolaminates can be used for the preparation of edible coatings and films which are currently used in the food industry such as fruit, vegetables, meats, chocolate, candies, bakery products and French fries. These coatings or films could be used as barriers to moisture, lipid, gases and increase the textural properties of foods, or applied as carriers of functional agents including colors, flavors, antioxidants, nutrients, and antimicrobials (Phan et al. 2008; Ponce et al. 2008; Cha and Chinnan 2004; Rhim 2004).

Silver colloids, silver nanoparticles have been found to be effective against numerous species of bacteria, including: *E. coli*, *Enterococcus faecalis*, *Staphylococcus* (*aureus* and *epidermidis*), *Vibrio cholera*, *Pseudomonas* (*aeruginosa*, *putida*, *fluorescens*), *Shigella flexneri* , *Bacillus* (*anthracis*, *subtilis* and *cereus*), *Proteus mirabilis*, *Salmonella enteric Typhimurium*, *Micrococcus luteus*, *Listeria monocytogenes* and *Klebsiella pneumoniae* (Panacek et al. 2006; Eby et al. 2009; Egger et al. 2009; Fayaz et al. 2010; Duncan 2011). Silver nanoparticles are also effective against strains of these organisms that are resistant to potent chemical antimicrobials, vancomycin-resistant *Enterococcus* and extended- spectrum b-lactamase. In addition, silver nanoparticles are toxic to fungi (e.g.,*Candida albicans*, *Aspergillus niger*, *Trichophyton mentagrophytes* (Kim et al. 2009; Duncan 2011).

2.2.11 Nanotechnology Based Cosmeceuticals

Cosmeceutical is defined as a product between a drug and cosmetics and cosmeceuticals are the fastest growing segment of the personal care industry (Fulekar 2010). Liposomes are used in a variety of cosmeceuticals because they are biocompatible, biodegradable, nontoxic, flexible vesicles and can encapsulate active ingredients easily and liposomes can protect the encapsulated drug from external environment. One of the main ingredients of liposome is phosphatidylcholine which has been used in skin care products (moisturizer, lotions, creams, etc.) and hair care products (shampoo, conditioner) due to its softening and conditioning properties. Several active ingredients (e.g., vitamins A, E, and K) and antioxidants (e.g. carotenoids, lycopene and CoQ10) have been incorporated into liposomes which increases their physical and chemical stability when dispersed in water (Müller-Goymann 2004; Nandita et al. 2016a).

Various nanotechnology-based cosmeceutical products are in the market used as moisturizer, cleanser, antiwrinkle, antiaging, sunscreen manufactured by Lancôme, Kara Vita, Nano-Infinity Nanotech, L'Oreal companies (Lohani et al. 2014).

2.3 Intellectual Property Rights in Nanotechnology

2.3.1 Intellectual Property Rights Types

It includes patents, copyright, industrial design rights, trademarks, plant variety rights, trade dress, and trade secrets explained as follows:

2.3.1.1 Patent

A patent is a form of right granted by the government to an inventor, giving the owner the right to exclude others from making, using, selling, offering to sell, and importing an invention for a limited period of time, in exchange for the public disclosure of the invention. An invention is a solution to a specific technological problem, which may be a product or a process and generally has to fulfil three main requirements: it has to be new, not obvious and have an industrial application.

2.3.1.2 Copyright

A copyright gives the creator of original work exclusive rights to it, usually for a limited time. Copyright may apply to a wide range of creative, intellectual, or artistic forms, or “works”. Copyright does not cover ideas and information themselves, only the form or manner in which they are expressed (Stokes 2001).

2.3.1.3 Industrial Design Right

An industrial design right (sometimes called “design right”) protects the visual design of objects that are not purely utilitarian. An industrial design consists of the creation of a shape, configuration or composition of pattern or color, or combination of pattern and color in three-dimensional form containing aesthetic value. An industrial design can be a two- or three-dimensional pattern used to produce a product, industrial commodity or handicraft.

2.3.1.4 Plant Breeders’ Rights

Plant breeders’ rights or plant variety rights are the rights to commercially use a new variety of a plant. The variety must amongst others be novel and distinct and for registration the evaluation of propagating material of the variety is examined.

2.3.1.5 Trademark

A trademark is a recognizable sign, design or expression which distinguishes products or services of a particular trader from the similar products or services of other traders.

2.3.1.6 Trade Dress

Trade dress is a legal term of art that generally refers to characteristics of the visual appearance of a product or its packaging (or even the design of a building) that signify the source of the product to consumers: Merges et al. (2007).

2.3.1.7 Trade Secrets

A trade secret is a formula, practice, process, design, instrument, pattern, or compilation of information which is not generally known or reasonably ascertainable, by which a business can obtain an economic advantage over competitors or customers.

2.3.2 Issues and Challenges

The huge investment in nanotechnology research should accelerate the availability of commercial nanotechnology applications but patenting nanotechnology inventions is more problematic than other inventions due to following issues (Barpujari 2010):

2.3.2.1 Broad Claims and Patents on Basic Inventions

Since a single invention could be used for a broad range of applications, the patentee tries to maximize the profit by preferring patent claims which cover many applications and markets as possible. Due to the constraint of well versed examiners at patent offices, these types of applications face problem of rejections despite of overly broad claims.

2.3.2.2 Multi-disciplinary and Multi-industrial Applications

One distinguishing feature of nanotechnology inventions is their multi-disciplinary nature; most of them involve a vast range of disciplines such as chemistry, biology, physics, pharmaceuticals, computer science, material science and other disciplines.

They may also have broad spectrum of industries due to size of nanoparticles e.g. carbon nanotubes (nanomaterial) have applications in energy, electronics, materials and life sciences industries due to their unique electrical, mechanical, thermal and optical properties.

2.3.2.3 Difficulties in Identifying Nanotechnology Patents

The broad definition of nanotechnology creates difficulties for both the inventor and the patent examiner in classifying new inventions for patent office. A patent application may use terms such as ‘microscale’ and ‘quantum dots’ to describe nanotechnology invention instead of using term nanotechnology. Therefore both inventor and the examiner must take precaution in searching the term in prior art in nanotechnology area.

2.3.2.4 Difficulties in Fulfilling Patentability Criteria

A patent can only be obtained on an invention if claims are novel, non- obvious over the prior art and have an industrial application. The novelty and inventive step requirement have created difficulties for nano-patents even in United States.

2.3.3 Global Scenario of Nanotechnology Patents

Inventions reflected by the number of patent applications filed in the top 50 depositories was about 13,000 in 2008 as compared to about 1200 in year 2000 (Huang et al. 2004, 2005).

A study on Indian publications and patents in nanotechnology during 1990–2007 (in foreign patent office’s like the United States Patent and Trade Office, European Patent Office, Japan Patent Office etc.) arrived at the following conclusions (Gupta 2008):

- Of the total 167 patents, 64 patents (39 % of the total patents) are owned by government institutions, 45 patents (27 % of the total) by firms in the industry and 10 patents (6 % of the total) by academic institutions. There are 37 patents (22 % of the total) that are owned by individual inventors. The remaining 5 % of the patents are joint patents in collaboration between government institutions or firms from industry.
- The leading contributors from the government sector include laboratories of the Council of Scientific and Industrial Research (CSIR), Defence Research and Development Organisation (DRDO)
- The academic institutions that have taken patents include the Indian Institute of Science, Indian Institutes of Technology and Jawahar Lal Nehru University.

Table 2.4 Top assignees in 2011 nanotechnology patent literature by healthcare and medicine sector

S.No.	Company	Country
1	GeneASys	Australia
2	Boston Scientific	United States
3	Merck	United States
4	Abbott Laboratories	United States
5	Life Technologies Corporation	United States

Jordan et al. (2012)

- Firms like Ranbaxy Laboratories, Stempeutics Research Private Limited, Panacea Biotech Limited and Arrow Coated Products Limited are the leading owners of industry patents.
- Academic institutions have more number of publications than patents while reverse is true for industry.

The annual rate of increase for all the patent publications is more pronounced between 2000 and 2008 (34.5 %). This rate is higher than that of Science Citation Index's article publication rate of 20–25 % for the same period when we use the same keyword "title–abstract" search approach as for patent applications (Dang et al. 2010). Top assignees in nanotechnology patent literature by medicine sector are described in Table 2.4.

Nanotechnology emerged as an advance discipline in twentieth century and now progressing by leaps and bounds. Unite States ranks first position among top 20 countries while India stands on nineteenth position for filing United States Patent and Trade Office patents related to nanotechnology as shown in Table 2.5. In scientific publications related to nanotechnology Unite States ranks first position among top 20 countries while India stands on eighth position (Chen et al. 2013).

2.3.4 Copyright, Trademarks and Designs Protection for Nanotechnology

2.3.4.1 Copyright Protection for Nanotechnology

Copyright protects a wide range of subject matter or works, it has been suggested that a molecular architecture of nanotechnology may be protected under Canadian copyright law. Different types of original work are protected provided they are within the categories specified in the Malaysian and UK Copyright Acts, as well as meeting the requirements of originality and expression in material form. Copyright-protected works include literary, artistic, musical and dramatic and other works such as sound recordings, films, broadcasts, and performer's rights. The presumption can be made that the categories of work most relevant to nanotechnology are artistic and literary works (Norain 2012).

Table 2.5 USPTO patents filed by top 20 countries during 1991–2012

S.No.	Country	Total patents	1991–2000	2001–2010	2011–2012
1	United States	23,070	3597	13,947	5526
2	Japan	3332	534	1983	815
3	Korea (South)	1901	32	1114	755
4	Taiwan	1170	62	521	587
5	Germany	1079	119	687	273
6	France	799	160	396	243
7	China	591	1	262	328
8	Canada	408	56	256	96
9	Netherlands	349	30	198	121
10	Switzerland	284	61	156	67
11	Australia	218	28	144	46
12	UK	216	29	142	45
13	Israel	211	17	150	44
14	Sweden	165	21	100	44
15	Italy	161	24	109	28
16	Belgium	144	15	93	36
17	Singapore	126	2	90	34
18	Finland	72	8	43	21
19	India	60	2	28	30
20	Denmark	46	15	28	3

2.3.4.2 Trademarks Protection for Nanotechnology

A team from Monash University has created electron beam lithography instrument that managed to write or mark nano-sized objects or surfaces to a size less than 10 nm (Press Release 2009). Thus it is possible to mark products at nanoscale, though visualisation techniques such as atomic force microscopy and scanning tunneling microscope are needed to interpret them. Macro marks on packaging can be used to signify the source of nano products or services.

The law that governs trade mark registration in Malaysia is the Trade Marks Act 1976 and Trade Marks Regulations 1983, both came into effect on 1 September 1983. Trade Marks Act 1976 defines ‘mark’ to include a device, brand, heading, label, ticket, name, signature, word, letter, numeral etc. Visual perception which makes it difficult for Malaysian law to be applied to nanotechnology, as nanotechnology cannot be seen by the naked eye. Eligibility for protection of non-visible but perceptible marks such as smells and sounds provides a good consideration on how nanoscale marks may attract trademarks protection. Indeed, nanotechnology may help to deliver smell mark; nano-encapsulation methods are available for production of aromatic compounds in perfumes using nanoparticles such as gold-palladium. Nano-encapsulated fragrance may be embedded for example into textiles, shoes and other materials such as ceramics.

2.3.4.3 Design Protection for Nanotechnology

Design protection is arguably available to protect nanotechnology features although the arguments experience some difficulties. The argument is that not only the nature of nanotechnology itself, and its suitability as subject-matter, but also the inherent nature of overlapping rights in the intellectual property rights regimes as well as complexity in the design law protection itself, pose problems. In Malaysia, the protection of industrial design is provided under the Industrial Design Act 1996, or under copyright law. Examples of design may be appearance of devices such as nano-bots, or nano-robotics systems in medicine, the functional design of orthopaedic devices for arms and joint replacement, the molecular design that mimics nature called “bio-mimetic”, and the design of bio-compatible dendrimers for cancer diagnosis. The non-visibility of nano-creations has indicated that it was unfortunate to be protected under design law in Malaysia. Even in the UK/EU law, the protection provided under design is complex not only within different protection under design law itself but also overlapping rights with other intellectual property rights. Under UK registered design, the requirement that the design does not mean to be visible to the eye explained some favourable treatment to protect nano-creations. However, non-visibility and technical characteristics of nanotechnology proved to be less relevant to be protected under registered design/community (Norain 2012).

2.4 Conclusion

Nanotechnology is widely used in various fields such as medical, agricultural, industrial etc. due to the specific attributes of nanomaterials. Despite of worldwide applications of nanotechnology it faces many problems related to patenting due to broad claims, multidisciplinary applications, and difficulties in identifying nanotechnology patents and fulfilling patentability criteria. The 21-year evolution of nanotechnology reflected in United States Patent and Trade Office patents and scientific publications shows patents and research papers increased in 2001–2010 four times, while the 2-year 2011–2012 increases are two times approximately. Unite States ranks first position among top 20 countries for filing patents and publications related to nanotechnology while India stands on nineteenth position for filing patents and eighth position in scientific publications.

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Chapter 3
Green Synthesis and Spectroscopic Characterization of Nanoparticles

Ashutosh Kumar Shukla and Siavash Iravani

Abstract Nanoparticles have many applications in different fields including food and agriculture. Synthesis and characterization of nanoparticles have therefore attracted interest of scientific community. Here we review green methods of synthesis of metal and metal oxide nanoparticles. We describe synthesis using enzymes, monosaccharides, polysaccharides and biodegradable polymers. We explain the role of vitamins as reducing and capping agents in green synthesis of nanoparticles. Microwave assisted synthesis and biobased methods have also been illustrated with examples. We then discuss nanoparticle characterization using UV-Visible spectroscopy and Fourier-transform infrared spectroscopy. Applications in diverse fields including water purification are then highlighted.

Keywords Nanoparticles • Green synthesis • UV-visible spectroscopy • FT-IR spectroscopy • Water purification • Vitamin • Microwave • Bacteria • Fungi • Yeast

3.1 Introduction

Nanomaterials have enhanced surface to volume ratio as compared to macromaterials and therefore a smaller mass of material is required to achieve the same objective (Crane and Scott 2012; Masciangioli and Zhang 2003). Properties of nanoparticle-containing materials are quite different to those of their bulk counterparts (El-Sayed 2001). Nanoparticles have attracted considerable interest recently in the field of food, agriculture and pharmaceuticals (Dasgupta et al. 2015a; Nandita et al. 2015; Shivendu et al. 2014; Aditi et al. 2016). Improved antioxidant and antimicrobial activity of nanoemulsions leading to potential application in increasing the shelf life

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of fruit juice has also been recently reported (Dasgupta et al. 2015b). Possibility of use of iron nanoparticles to remove contamination from water and soil is reported by Crane and Scott (2012). A process to prepare silver– silica nanocomposite for treatment of waste water is also reported by Das et al. (2013).

Factors mentioned above are few of the many due to which nanoparticle research has attracted the focus of the masses in general and scientific community in particular in present times. There are different methods possible for synthesis of nanoparticles. Green synthesis of nanoparticles has become important due to environmental concerns related with chemical methods of synthesis. Optimum use/application of nanoparticles for specific purpose depends completely on the detailed information obtainable from different characterization techniques. Therefore, we have made an attempt to review the current trends in the green synthesis and spectroscopic characterization of nanoparticles. We have also emphasized some most relevant applications of nanoparticles so prepared and the future scope in this area.

3.2 Green Methods for Synthesizing Metal and Metal Oxide Nanoparticles

Green synthesis of nanoparticles using naturally occurring biodegradable materials such as enzymes, vitamins, polysaccharides, plant extracts, biodegradable polymers, and microorganisms is a very promising area in nanobiotechnology and green nanotechnology. There has always been a demand for reliable and eco-friendly processes to manufacture metal and metal oxide nanoparticles minimizing or even eliminating the use of toxic and hazardous chemicals. The only way to develop these “green” processes is to adapt benign synthesis approaches that use mild reaction conditions and non-toxic reaction precursors (Iravani 2011; Iravani and Zolfaghari 2013; Korbekandi et al. 2013; Korbekandi and Iravani 2013; Korbekandi et al. 2009, 2012). This section presents an overview of nanoparticle preparation by “Green chemistry” approaches which have advantages over conventional methods involving chemical agents associated with environmental toxicity (e.g., biocompatibility, biodegradability, cost-effectiveness and renewability).

3.2.1 Enzymes

Enzymatic method as a green approach has been used for synthesis of metal and metal oxide nanoparticles. This method has advantages over other biological methods as enzymes are available in pure form and their structures are also well known. For instance, silver nanoparticles were synthesized by an enzyme-induced growth process on solid substrates. Variations in the silver-nanoparticle films depending on the conditions during synthesis were observed. After an initial growth state, silver nanoparticles exhibited the so-called desert-rose or nanoflower-like structure

(Schneidewind et al. 2012). Moreover, exposing the silver ions to *Verticillium* resulted in the reduction of the silver ions and formation of nanoparticles. The enzymes in the cell wall membrane reduce the silver ions (Mukherjee et al. 2001).

Manivasagan et al. (2015) reported the production of α-amylase for extracellular synthesis of gold nanoparticles using *Streptomyces* sp. MBRC-82. The particles were synthesized using the optimized enzyme activity (~20–80 nm). Furthermore, Rangnekar et al. (2007) attributed the synthesis of gold nanoparticles to the presence of enzyme α-amylase. They reported the generation of gold nanoparticles, using a pure enzyme for the reduction of $AuCl^{4-}$, with the retention of enzymatic activity in the complex. The presence of free and exposed S−H groups was essential in the reduction of $AuCl^{4-}$ to gold nanoparticles. In this study, structural analysis of the enzymes showed that both α-amylase and EcoRI enzymes have free and exposed S−H groups in their native form and thus are suitable for the generation of nanoparticles. In another study, Kalishwaralal et al. (2010) studied the optimization of α-amylase production for the green synthesis of gold nanoparticles (~10–50 nm) by *Bacillus licheniformis*. This bacterium is known to synthesize amylase enzyme which is active in a wide range of temperature and pH (Khemakhem et al. 2009). In this study, response surface methodology and central composite rotary design (CCRD) were employed to optimize a fermentation medium for the production of α-amylase by *B. licheniformis* at pH 8. The three variables involved in the study of α-amylase were fructose, peptone and soya meal. Only fructose had a significant effect on α-amylase production. The most optimum medium containing (%) fructose: 3, peptone: 1, soya meal: 2, resulted in amylase activity of 201.381 U/ml (Kalishwaralal et al. 2010).

The enzyme α-amylase was used for the green synthesis of titanium dioxide nanoparticles (as the reducing and capping agent). Transmission electron microscopy (TEM) data showed that the morphology of produced nanoparticles depended upon the used enzyme concentration. The produced nanoparticles were investigated for their antibacterial effect on *Staphylococcus aureus* and *Escherichia coli* (Minimum inhibitory concentration (MIC) = 62.50 μg/ml). Jayaseelan et al. (2013) reported the green synthesis of titanium dioxide nanoparticles using *Aeromonas hydrophilla*. The gas chromatography – mass spectrometry (GC-MS) analysis of the broth showed the major compound found in the *A. hydrophilla* was glycyl-proline and other compounds present in lesser amounts areuric acid, glycl-glumatic acid, and Leucyl-leucine and compounds containing –COOH and –C=O group. They concluded that glycil-Lproline acted as reducing agent for the synthesis of titanium dioxide nanoparticles and the water soluble carboxylic acid compounds acted as stabilizing agents (Jayaseelan et al. 2013).

3.2.2 Monosaccharides and Polysaccharides

Monosaccharides and polysaccharides including plant polysaccharides (starch, cellulose, dextran, and alginic acid), mammalian glycosaminoglycan polysaccharides, heparin or hyaluronic acid and chitosan can be used for cost-effective, biocompatible, biodegradable and green synthesis of metallic nanoparticles. For example, silver nanoparticles were prepared using water as an eco-friendly solvent and polysaccharides as capping/reducing agents (Sathishkumar et al. 2009b). Actually, polysaccharides have functionalities including hydroxyl groups and a hemiacetal reducing end which are capable of reducing precursor salts. The oxidation of polysaccharide hydroxyl groups to carbonyl groups plays a critical role in bioreduction of gold salts (Mata et al. 2009). Furthermore, the reducing end of polysaccharides can also be used to introduce an amino functionality capable of complexing to and stabilizing metal nanoparticles (Nadkarni et al. 1994).

Starch is a mixture of α-amylose and amylopectin. Starch-stabilized and glucose-reduced silver nanoparticles were prepared via the incubation of silver salt with starch and glucose at 40 °C for 20 h producing a particle with a mean size of 5.3 nm (Raveendran et al. 2003b). The produced silver nanoparticles were stable without any noticeable aggregation even after 2 months of storage. Another thermal method, an autoclaving method (15 psi, 121 °C, 5 min), was introduced for the synthesis of stable face-centred cubic silver nanoparticles in the size range of 10–34 nm using soluble starch as both a reducing and stabilizing agent (Vigneshwaran et al. 2006). In another study, silver nanoparticles were prepared using starch under sonication. TEM images indicated the formation of spherical, polydispersed, amorphous, silver nanoparticles (~23–97 nm). Selected area electron diffraction (SAED) confirmed partial crystalline and amorphous nature of silver nanoparticles. The optimized reaction conditions include 10 ml of 1 mM $AgNO_3$, 25 mg starch, 11 pH range, and sonication for 20 min at room temperature (Kumar et al. 2014).

In one study, synthesis of starch-silver nanoparticles was carried out with starch (as a capping agent) and β-D-glucose (reducing agent) in a gently heated system (Raveendran et al. 2003a). The binding interactions between starch and the produced silver nanoparticles were weak and could be reversible at higher temperatures, allowing separation of the synthesized nanoparticles. In dual polysaccharide function, silver nanoparticles were synthesized by reduction of silver ions inside of nanoscopic starch templates (Raveendran et al. 2003a, 2005). The extensive network of hydrogen bands in templates provided surface passivation or protection against nanoparticle aggregation. Green synthesis of silver nanoparticles using negatively charged heparin (reducing/stabilizing agent and nucleation controller) was also reported by heating a solution of silver nitrate and heparin to 70 °C for about 8 h (Huang and Yang 2004). TEM micrographs demonstrated an increase in particle size of silver nanoparticles with increased concentrations of silver nitrate (substrate) and heparin. Moreover, changes in heparin concentration varied the morphology and size of silver nanoparticles. The synthesized silver nanoparticles were highly stable, and showed no signs of aggregation after 2 months (Huang and Yang 2004). In another study, stable silver nanoparticles (~10–34 nm) were synthesized by autoclaving a solution of silver nitrate (substrate) and starch (capping and reducing agent) at 15 psi and 121 °C for 5 min (Vigneshwaran et al. 2006). These nanoparticles were stable in solution for 3 months at about 25 °C. Smaller silver nanoparticles ($\leq$10 nm) were synthesized by mixing two solutions of silver nitrate containing starch (capping agent), and NaOH solutions containing glucose (reducing agent) in a spinning disk reactor with a reaction time of less than 10 min (Tai et al. 2008). Silver nitrate, glucose, sodium hydroxide, and starch could be used, respectively, to serve as precursor, reducing agent, accelerator, and stabilizer for the reduction synthesis of silver nitrate. Polyethylene glycol (reducing agent and stabilizing agent) was used to prepare stable monodispersed silver colloids (~10 nm) (Bo et al. 2009). Biodegradable starch served as a stabilizing agent to synthesize silver nanoparticles (~5–20 nm). According to High-resolution transmission electron microscopy (HR-TEM) findings, silver nanoparticles were covered by starch layer and formed spherical core-shell silver/starch nanoparticles. In addition, X-ray diffraction (XRD) confirmed the presence of silver nanoparticles with face-centered cubic structure (Gao et al. 2011).

Hydroxypropyl starch can be used as a reducing and stabilizing agent in the synthesis of stable silver nanoparticles (~6–8 nm) with no aggregation for more than 6 months. In addition, the influences of the reaction parameters, such as the concentrations of hydroxypropyl starch and $AgNO_3$, pH, temperature, and duration of the reaction medium on the size and agglomeration of the formed silver nanoparticles were studied (El-Rafie et al. 2011). Hydroxypropyl cellulose can also be used to manufacture silver nanoparticles and as a dopant for visible light active titanium dioxide. Therefore, optimum conditions for silver nanoparticles preparation were pH 12.5, 0.3 % hydroxypropyl cellulose solution having molar substitution of 0.42 and carrying out the reaction at 90 °C for 90 min. On the other hand, doped-TiO_2 nanoparticles were prepared using a benign "one-pot" synthesis procedure at room temperature, resulting in stable and effective nanoparticles with average size of 17 nm and Brunauer-Emmett-Teller (BET) surface area of 133.8 $m^2\ g^{-1}$ which were efficient in degrading organic contaminants in the visible-light range (Virkutyte and Varma 2013; Abdel-Halim and Al-Deyab 2011).

3.2.3 *Biodegradable Polymers*

Polymers with ion-exchangeable capacity can be used in the fields of nanoscience. The polymer often used contained phosphonic acid groups and had a low molecular weight. For instance, silver nanoparticles were stabilized in the presence of an ion-exchange polymer. The surface morphology indicated that cubes and rectangular prism structures were formed (García-Serrano et al. 2011). Co-polymers like cyclodextrin, grafted with poly acrylic acid, were used to produce silver nanoparticles where potassium per sulfate was used as the initiator. The co-polymer reduced and stabilized silver ions, which yielded silver nanoparticles. Concentrations of the alkali, silver nitrate, the co-polymer, and the method of heating, all played an important role in determining the size of the produced nanoparticles (Hebeish et al. 2011).

Poly(methyl vinyl ether-co-maleic anhydride) was used as a reducing and stabilizing agent as well. The produced nanoparticles were stable at room temperature for up to a month and had a 5–8 nm coat of Poly(methyl vinyl etherco-maleic anhydride) surrounding them (Maity et al. 2011). It was reported that the nanoparticles

(~10.2–13.7 nm) were fcc structures, non-aggregating, and very spherical in shape (Medina-Ramirez et al. 2009). Sarkar et al. (2010) examined the synthesis of silver nanowires and nanoparticles. Through a polypol process, with the help of a polymer, silver nanowires and nanoparticles were formed. It was reported that the nanoparticles were 60–200 nm in size and held prismatic and hexagonal shapes while the nanowires had diameters from 50 to 190 nm and lengths between 40 and 1,000 μm. The reaction occurred at 210 °C when ethylene glycol was used as the solvent. Different photoluminescence emission from the nano-clusters spread out through methanol and ethylene glycol at room temperature. The excitation wavelengths were measured between 300 and 414 nm (Sarkar et al. 2010). By changing the reducing and capping agents used to synthesize silver nanoparticles, one can change morphologies of the nanoparticles, as well. The synthesis yielded nanoparticles which were spherical in shape and around 15–43 nm in size after being heated at 70 °C for 30 min; while at room temperature, the particles were only 8–24 nm. Sodium hydroxide reduced the salt in ethylene glycol and the cubes were formed upon some aggregation. By adding 5 wt.% polyvinylpyrrolidone to 1 wt.% of starched solution (aq), mixtures of spherical and anisotropic structures were produced. The reaction took place at 70 °C for 1 h (Shervani et al. 2008).

3.2.4 Vitamins

Silver nanoparticles were prepared from silver nitrate in the presence of vitamin C derivative 6-palmitoyl ascorbic acid-2-glucoside (PAsAG), via a sonochemical route (Chandrasekharan et al. 2011). Ag-PAsAG nanocomplex with average size of 5 nm was formed and used to protect DNA from γ-radiation-induced damage. It was reported that the presence of Ag-PAsAG complexes during irradiation inhibited the disappearance of covalently closed circular form of plasmid pBR322 with a dose-modifying factor of 1.78. Ag-PAsAG protected cellular DNA from radiation-induced damage as evident from comet assay study on mouse spleen cells, irradiated ex vivo (Chandrasekharan et al. 2011). Moreover, Huang et al. (2007) fabricated gold nanodogbones with simple seeded mediated growth method in the presence of vitamin C. It was reported that the morphologies of the formed nanoparticles highly depended on the amount of added vitamin C (10–40 mL). In another study, monodispersed silver nanoparticles were synthesized by a simple one-step procedure in the alkaline sub-phase beneath vitamin E Langmuir monolayers. It was reported that the phenolic groups in vitamin E molecules were converted to a quinone structure, and the silver ions were mainly reduced to ellipsoidal and spherical nanoparticles. According to the electron-diffraction pattern, silver nanoparticles were face-centered cubic polycrystalline (Zhang et al. 2006).

In addition, vitamin B2 was also reported to be an effective reducing as well as capping agent due to its high water solubility, biodegradability and low toxicity in comparison to other available reducing agents (Nadagouda and Varma 2008a). In one study, green synthesis of silver and palladium nanospheres, nanowires, and nanorods by using vitamin B2 (as reducing and capping agent) has been reported. Importantly, the addition of a solvent along with B2 may alter the sizes of resulting nanoparticles. The average particle size of nanoparticle was found to be silver (~6.1 ± 0.1 nm) and palladium (~4.1 ± 0.1 nm) nanoparticles in ethylene glycol, and silver (~5.9 ± 0.1 nm, and 6.1 ± 0.1) nanoparticles in acetic acid and N-methylpyrrolidinone, respectively. Interestingly, when water was used as a solvent, silver and palladium nanoparticles were self-assembled into rod-like structures. However, in isopropanol, the nanoparticles yielded wire-like structures with a thickness in the range of 10–20 nm and several hundred micrometers in length. Finally, in acetone and acetonitrile, the silver and palladium nanoparticles were self-assembled into a regular pattern making nanorod structures with thicknesses ranging from 100 to 200 nm and lengths of a few micrometers (Nadagouda and Varma 2008a; Virkutyte and Varma 2013).

Nadagouda et al. (2009) reported a green one-step method to synthesize palladium nanobelts, nanoplates and nanotrees using vitamin B1. In this method, water was used as a solvent and vitamin B1 as a reducing agent. It was reported that palladium concentration affected the shapes and sizes of the produced nanostructures. A lower palladium concentration yielded a plate-like structure where thickness of these plates varied from 100 to 250 nm with a length of several microns. An increase in concentration of palladium resulted in the formation of tree-like structures. Upon further increase in palladium concentration, palladium nanoplates started becoming thicker by vertically aligning themselves together to form ball-like structures. The produced palladium nanoparticles showed excellent catalytic activity for several carbon-carbon bond forming reactions such as Suzuki, Heck and Sonogashira reactions under microwave irradiation conditions.

3.2.5 Microwave-Assisted Synthesis

Microwave-assisted synthesis is a promising method for synthesis of nanoparticles (Nadagouda et al. 2011). Silver, gold, platinum, and gold-palladium titanium dioxide nanostructures were prepared using microwave-assisted synthetic approaches (Shivendu et al. 2016). For instance, it was reported that silver nanoparticles could be synthesized by microwave-assisted synthesis method employing carboxymethyl cellulose sodium as reducing and stabilizing agent. The size was dependent on concentration of sodium carboxymethyl cellulose and silver nitrate (the substrate). The produced nanoparticles were uniform and stable at room temperature for 2 months without any visible changes (Chen et al. 2008). Production of silver nanoparticles in presence of Pt seeds, polyvinyl pyrrolidine and ethylene glycol was also reported (Navaladian et al. 2008). Furthermore, starch was employed as a template and reducing agent for synthesis of silver nanoparticles with an average size of 12 nm, using microwave-assisted synthetic method. Starch functions as a template, preventing the aggregation of the produced silver nanoparticles (Sreeram et al. 2008).

A bulk and shape-controlled synthesis of noble nanostructures with various shapes (e.g., prisms, cubes, and hexagons) occurs via microwave-assisted spontaneous reduction of noble metal salts using aqueous solution of α-D-glucose, sucrose, and maltose (Mallikarjuna and Varma 2007). The size of the produced nanoparticles can be controlled by varying the concentration of the sugars; higher concentration provides uniformly smaller size particles which increases with decrease in the concentration of the sugars.

Microwaves in combination with polyol process were applied for synthesis of silver nanospheroids using ethylene glycol and poly N-vinylpyrrolidone as reducing and stabilizing agents, respectively (Komarneni et al. 2002). In a typical polyol process, inorganic salt is reduced by the polyol (e.g., ethylene glycol which serves as both solvent and reducing agent) at a high temperature. Yin et al. (2004) reported that large-scale and size-controlled silver nanoparticles could be rapidly synthesized under microwave irradiation from an aqueous solution of silver nitrate and tri-sodium citrate in the presence of formaldehyde as a reducing agent. Size and size distribution of the produced silver nanoparticles were strongly dependent on the states of silver cations in the initial reaction solution. Silver nanoparticles with different shapes can be synthesized by microwave irradiation of a silver nitrate-ethylene-glycol-$H_2[PtCl_6]$-poly(vinylpyrrolidone) solution within 3 min (Tsuji et al. 2008).

3.2.6 Biobased Methods

3.2.6.1 Bacteria and Actinomycetes

Bacteria and actinomycetes are capable of reducing metal ions into metallic nanoparticles. For instance, Konishi et al. (2007) reported microbial deposition of gold nanoparticles by the metal reducing bacterium, *Shewanella algae*. They demonstrated that harvested cells of *S. algae* were capable of reducing 1 mM $AuCl^{4-}$ ions into elemental gold within 30 min at 25 °C over the pH range from 2.0 to 7.0, when H_2 gas was provided as the electron donor (Caccavo et al. 1992). At pH 7.0, biogenic gold nanoparticles (~10–20 nm), were deposited in the periplasmic space of *S. algae* cells. When the solution pH decreased to below 2.8, some gold nanoparticles were deposited extracellularly. At this pH, the biogenic gold nanoparticles (~15–200 nm), on the bacterial cells exhibited various morphologies. At a solution of pH 2.0, biogenic gold nanoparticles (~20 nm), were deposited on the bacterial cells, and larger gold particles approximately 350 nm in size were deposited extracellularly. Thus, it could be concluded that the solution pH is an important factor in controlling the morphology of biogenic gold nanoparticles and in the location of gold deposition (Konishi et al. 2007). They observed that the decrease in the soluble Au (III) concentration was presumably caused by its rapid reduction into insoluble gold. In the absence of H_2 gas, however, *S. algae* cells were not able to reduce Au (III) with lactate as an alternative electron donor. Moreover, in a sterile control medium without *S. algae* cells, Au (III) was not chemically reduced by H_2 gas.

Thus, resting cells of *S. algae* were able to reduce the soluble Au (III) into insoluble gold in the presence of molecular H_2 as the electron donor (Konishi et al. 2006; Kashefi et al. 2001). A number of metal-reducing bacteria have been isolated and characterized from a variety of habitats, and much work has been focused on *S. oneidensis* and *Geobacter* spp. (Lovley 2001).

Fe (Ш)-reducing bacteria and archaea, were capable of precipitating gold by reducing Au (Ш) to Au (0) (Kashefi et al. 2001). The reaction seemed to be enzymatically catalyzed which were dependent on temperature and the presence of a specific electron donor, hydrogen. It was reported that hyperthermophilic archaea, *Pyrobaculum islandicum*, *Pyrococcus furiosus* and the acetate-oxidizing hyperthermophilic strain 234, *Thermotoga maritime* and mesophilic bacteria, *S. algae* strain BRY, *Desulfovibrio vulgaris*, and *Geovibrio ferrireducens* were capable of reducing Au(Ш), while hyperthermophilic Archaea, *P. aerophillum*, *Archaeoglobus fulgidus*, *Ferroglobus placidus* and mesophilic bacteria, *D. palmitatis*, *Geothrix fermentans*, *Desulfitobacterium metallireducens* and *Geobacter sulfurreducens*, could not reduce Au(Ш) (Kashefi et al. 2001).

CdS nanoparticles can be biologically synthesized by using bacterial cells (Watson et al. 1999; Zhang et al. 1998; Lee et al. 2004). *Clostridium thermoaceticum* showed the ability to grow autotrophically on CO_2 and H_2, utilizing the so-called Wood-Ljungdahl pathway to synthesize acetyl coenzyme A (acetyl-CoA), a starting material for the anabolic processes of these cells (Barondeau and Lindahl 1997). Cunningham and Lundie (1993) reported that *C. thermoaceticum* was able to precipitate cadmium extracellularly at an initial concentration of 1 mM. This process was energy dependent and required cysteine. The yellow precipitate of CdS appeared approximately 12 h after the addition of $CdCl_2$ and complete removal of the metal from the growth medium was accomplished within 72 h. CdS was precipitated from $CdCl_2$ in the presence of cysteine hydrochloride by *C. thermoaceticum* at the cell surface and in the medium (Cunningham and Lundie 1993). *Rhodopseudomonas palustris* was capable of producing cadmium sulfide nanoparticles when it was incubated with 1 mM $CdSO_4$ at 30 °C for 72 h (Bai et al. 2009). The researchers of this study found that C-S-lyase (an intracellular enzyme located in the cytoplasm) was responsible for the synthesis of nanoparticles. One of the interesting results of this study was that *R. palustris* transported CdS nanoparticles out of the cell.

Labrenz et al. (2000) reported that spherical aggregates of 2–5 nm diameter sphalerite zinc sulfide (ZnS) particles were formed within natural biofilms dominated by sulfate-reducing bacteria of the family of Desulfobacteriaceae. A combination of geochemical and microbial processes led to zinc sulfidebio-mineralization in a complex natural system. It is appropriate to mention that the concentration of Zn was significantly reduced to below-acceptable levels for drinking water with the use of this method. *Rhodobacter sphaeroides* was developed for the synthesis of ZnS nanoparticles with an average diameter of 8 nm (Bai et al. 2006). ZnS and PbS nanoparticles (~10.5 ± 0.15 nm) were produced by using *R. sphaeroides* (Bai and Zhang 2009). It was revealed that culture time could control the size of the produced lead sulfide nanoparticles. Crystalline, needlelike deposits were formed around the cells of Pseudomonas aeruginosa in the presence of La $(NO_3)_2$ (Mullen et al. 1989).

Silver concentrations up to 25 % of the bacterial dry biomass were reached in a mixed culture of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* after leaching of a sulphide mineral (Pooley 1982). Brock et al. (1976) reported that *T. ferrooxidans*, *T. thiooxidans* and *Sulfolobus acidocaldarius* (thermophilic bacterium able to oxidize both sulfur (Brock et al. 1976) and ferrous iron (Shiwers and Brock 1973)) were able to reduce ferric ion to the ferrous state when growing on elemental sulfur as an energy source. *T. thiooxidans* was able to reduce ferric iron at low pH medium aerobically. The ferrous iron formed was stable to autooxidation and *T. thiooxidans* was unable to oxidize ferrous iron, but the reduction of ferric iron by using *T. ferrooxidans* was not aerobic because of the rapid bacterial reoxidation of the ferrous iron in the presence of oxygen (Brock and Gustafson 1976). This study reported that bacterial catalysis may play a significant role in the reactivity of ferric iron and the ability of bacteria to oxidize elemental sulfur using ferric iron as an oxidant. This could be geochemically significant in the leaching of sulfide ores and in the development of acid mine drainage (Brock and Gustafson 1976). Other biomineralization phenomena, such as the formation of tellurium in *E. coli* K12, the direct enzymatic reduction of Tc (VII) by resting cells of *Shewanella putrefaciens* and *Geobacter metallireducens* (previously known as strain GS-15) (Lloyd et al. 1999) and the reduction of selenite to selenium by *Enterobacter cloacea*, *D. desulfuricans* and *Rhodospirillum rubrum* (Kessi et al. 1999), have been reported, as well. Roh et al. showed that metals such as Co, Cr, and Ni might be substituted into magnetite crystals biosynthesized in the thermophilic iron-reducing bacterium *Thermoanaerobacter ethanolicus* (Klaus-Joerger et al. 2001; Yeary et al. 2005; Roh et al. 2001). This procedure led to formation of octahedral-shaped magnetite nanoparticles (<12 nm) in large quantities that co-existed with a poorly crystalline magnetite phase near the surface of the cells (Roh et al. 2001). A more fundamental investigation in the assembly of single-domain magnetite particles (Fe_3O_4) into folded-chain and flux-closure ring morphologies by harvested magnetotactic bacterium, *Magnetospirillum magnetotacticum*, was carried out by Philipse and Maas (2002). Magnetic nanoparticles were also assembled into ordered structures when the motion of *M. magnetotacticum* (MS-1) was controlled by applying a magnetic field (Lee et al. 2004).

Sulfate-reducing bacteria were capable of producing magnetic iron sulfide nanoparticles. Adsorption of radioactive metals by these magnetic iron sulfide nanoparticles occurred due to high surface area (400–500 m^2g^{-1}) which could provided a suitable matrix for the long-term safe storage of hazardous radioactive pertechnetate ion (Watson et al. 1999, 2001). GS-15 oxidized simple organic compounds such as acetate, butyrate, and ethanol to carbon dioxide with Fe (III) or Mn (IV) as the sole electron acceptor (Lovely et al. 1987; Lovley and Phillips 1988). Iron-reducing microorganism, GS-15, produced copious quantities of ultra fine-grained magnetite, with size range of 10–50 nm, under anaerobic conditions by coupling the organic matter to the reduction of ferric iron (Lovely et al. 1987). In this process, the non-magnetic brown amorphic ferric oxide was converted to a black solid material which was strongly attracted to a magnet. But, GS-15 was not magnetotactic because the crystals were clearly external to the cells and were not aligned in chains.

Lovely et al. (1989) investigated the ability of *Alteromonas putrefaciens* to couple the oxidation of potential electron donors (e.g., lactate, pyruvate, hydrogen and formate) to the reduction of Fe (III) and Mn (IV). Also they reported that *Pelobacter acetylenicus* and *P. venetianus* were able to reduce Fe (III). They demonstrated that *P. carbinolicus* was capable of conversing energy to support growth from Fe (III) respiration as it also grew with H_2 or formate as the electron donor and Fe (III) as the electron acceptor. *P. carbinolicus* grew with ethanol (ethanol was metabolized to acetate) as the sole electron donor and Fe (III) as the sole electron acceptor. Growth was also possible on Fe (III) with the oxidation of propanol to propionate or butanol to butyrate if acetate was provided as a carbon source (Lovley et al. 1995).

Green synthesis of titanium dioxide (TiO_2) nanoparticles was done using *Planomicrobium* sp. (Malarkodi et al. 2013). The produced nanoparticles exhibited antimicrobial activity against *B. Subtilis*, *K. planticola*, and *A. niger*. Furthermore, it was reported that *Shewanella sp.* strain PV-4 was able to reduce metals such as Fe (III), Co (III), Cr (VI), Mn (IV), and U (VI) as electron acceptors while using lactate, formate, pyruvate, or hydrogen as electron donors (Roh et al. 2006). Growth during iron reduction occurred over the pH range of 7.0–8.9, a sodium chloride range of 0.05–5 %, and a temperature range of 0–37 °C, with an optimum growth temperature of 18 °C. Strain PV-4 was able to reduce Fe (III)-citrate, as indicated by the color change of the culture solution from brownish gray [Fe (III)-citrate]sil to colorless at 8 °C. Strain PV-4 was also able to reduce Co(III) [Co(III)-EDTA] to Co(II), Cr(VI) (potassium chromate) to Cr(III), and U(VI) (uranyl carbonate) to U(IV) with lactate (10 mM) as the electron donor, as indicated by the color change of the culture solution from purple[Co(III)-EDTA] and yellow (potassium chromate and uranyl carbonate) to colorless at 8 °C. Furthermore, the strain PV-4 was able to reduce manganese oxide using lactate (10 mM) as an electron donor and formed rhodochrosite ($MnCO_3$) at 8 °C under an H_2-CO_2 atmosphere. However, the cells did not reduce Fe (III)-EDTA as an electron acceptor using lactate (10 mM) as the electron donor at 8 °C under N_2 atmosphere. Moreover, *D. desulfuricans* was capable of enzymatic reduction of U (VI) (Lovley and Phillips 1992; Mohagheghi et al. 1985; Woolfolk and Whiteley 1962). When washed cell suspensions of *D. desulfuricans* were suspended in bicarbonate buffer containing lactate or hydrogen as the potential electron donor, U (VI) concentration was decreased and amount of U (IV) concentration was increased (Lovley and Phillips 1992). Enzymatic reduction of U (VI) by *D. desulfuricans* was much faster than non-enzymatic reduction of U (VI) by sulfide (Mohagheghi et al. 1985), even when cells of *D. desulfuricans* were added to provide a potential catalytic surface for the nonenzymatic reaction (Lovley and Phillips 1992). Microbial reduction of soluble U (VI) to insoluble U (IV) may play an important role in the geochemical cycle of uranium and serve as a mechanism for the bioremediation of uranium-contaminated waters, as well (Lovley et al. 1991). Reductive precipitation of uranium might also account for the ability of the bottom sediments of algal ponds to remove dissolved uranium from uranium mine wastewaters (Brierley and Brierley 1980). Bioreactors containing U (VI)-reducing microorganisms (such as cells and S-layer proteins of *Bacillus sphaericus* JG-A12 (Pollmann et al. 2006)), could rapidly remove dissolved uranium from water (Gorby and Lovley 1991); therefore, *D. desulfuricans* might show useful and potential capabilities for recycling and recovering uranium from contaminated waters and waste waters (Lovley and Phillips 1992).

3.2.6.2 Yeasts and Fungi

Several studies indicated that yeasts extracts could be used to synthesize metallic nanoparticles. For instance, Kowshik et al. (2003) demonstrated the extracellular formation of silver nanoparticles (~2–5 nm) by a silver-tolerant yeast strain MKY3. Furthermore, *Saccharomyces cerevisae* broth was used to synthesize gold and silver nanoparticles. The produced gold nanoparticles (20–100 nm, pH 4–6) and silver (10–20 nm, pH 8–10) were formed extracellularly within 24 h and 48 h, respectively (Lim et al. 2011). Kumar et al. (2011) showed the applicability of yeast species *Hanensula anomala* to reduce gold salt in the presence of amine-terminated polyamidoamine dendrimer as the stabilizer; cysteine could also be used as stabilizer. Furthermore, *Candida guilliermondii* was used to prepare silver (~10–20 nm) and gold nanoparticles (~50–70 nm) (Mishra et al. 2011). The produced nanoparticles were tested against five pathogenic bacterial strains. The highest efficiency for both gold and silver nanoparticles was observed against *S.aureus*, which indicated the applicability of yeast-synthesized nanoparticles for environmental remediation and medical fields (Mishra et al. 2011).

Spherical and occasionally triangular silver nanoparticles (~5–50 nm) were biologically synthesized using *Fusarium oxysporum*, with no evidence of flocculation of the particles even a month after the reaction (Ahmad et al. 2003a). The long-term stability of the nanoparticle solution might be due to the stabilization of the silver particles by proteins. Silver nanoparticles have been reported to interact strongly with proteins including cytochrome c (Cc). This protein could be self-assembled on citrate-reduced silver colloid surface (Macdonald and Smith 1996; Nandita et al. 2016; Shivendu et al. 2015). Interestingly, adsorption of (Cc)-coated colloidal gold nanoparticles onto aggregated colloidal Ag resulted Ag: Cc: Au nanoparticle conjugate (Keating et al. 1998). In UV-vis spectra from the reaction mixture after 72 h, the presence of an absorption band at ca. 270 nm might be due to electronic excitations in tryptophan and tyrosine residues in the proteins. In the case of *F. oxysporum*, the biological reduction of silver ions was attributed to an enzymatic process involving NADH-dependent reductase (Ahmad et al. 2003b). The exposure of silver ions to *F. oxysporum* resulted in release of nitrate reductase and subsequent formation of highly stable silver nanoparticles in solution (Kumar et al. 2007). The secreted enzyme was found to be dependent on NADH cofactor. High stability of the produced nanoparticles in solution was due to capping of particles by release of capping proteins by *F. oxysporum*. Moreover, stability of the capping protein was found to be pH dependent. At higher pH values (>12), the nanoparticles in solution remained stable, while they aggregated at lower pH values (<2) as the protein was denatured. Kumar et al. (2007) demonstrated enzymatic synthesis of silver nanoparticles with different chemical compositions, sizes and morphologies, using α-NADPH-dependent nitrate reductase purified from *F. oxysporum* and phytochelatin, in vitro. Silver ions were reduced in the presence of nitrate reductase, leading to formation of a stable silver hydrosol 10–25 nm in diameter and stabilized by the capping peptide. Use of a specific enzyme in in vitro synthesis of nanoparticles showed interesting advantages. This would eliminate the downstream processing required for the use of these nanoparticles in homogeneous catalysis and other applications such as non-linear optics. The biggest advantage of this protocol based on purified enzyme was the development of a new approach for green synthesis of nanomaterials over a range of chemical compositions and shapes without possible aggregation. Korbekandi et al. (2013) demonstrated the bioreductive synthesis of silver nanoparticles using *F. oxysporum*. Previous researchers reported qualitative production of silver nanoparticles by *F. oxysporum*, but they did not optimize the reaction mixture. In Scanning electron microscope (SEM) micrographs, silver nanoparticles were almost spherical, single (~25–50 nm) or in aggregates (100 nm), attached to the surface of biomass. The biological reduction of metal ions and stabilization of the silver nanoparticles was confirmed to occur by an enzymatic process. It seems that the first step involves trapping of the Ag^+ ions by *F. oxysporum* cells. Furthermore, Ingle et al. (2008) demonstrated the potential ability of *Fusarium acuminatum* Ell. and Ev. (USM-3793) cell extracts in biosynthesis of silver nanoparticles. The nanoparticles produced within 15–20 min and were spherical with a broad size distribution in the range of 5–40 nm with the average diameter of 13 nm. A nitrate-dependent reductase enzyme might act as the reducing agent. The white rot fungus, *Phanerochaete chrysosporium*, also reduced silver ions to form nano-silver particles (Vigneshwaran et al. 2006). The most dominant morphology was pyramidal shape, in different sizes, but hexagonal structures were also observed. Moreover, silver nanoparticles were synthesized using *Aspergillus flavus*. The prodeced nanoparticles were found to be stable in water for more than 3 months with no significant aggregation because of surface binding of stabilizing materials secreted by the fungus (Vigneshwaran et al. 2007). Extracellular biosynthesis of silver nanoparticles (~5–25 nm) using *Aspergillus fumigatus* has also been investigated (Bhainsa and D'Souza 2006). Most of the nanoparticles were spherical in nature with some others having occasionally triangular shapes.

The extracellular filtrate of *Cladosporium cladosporioides* biomass was used to synthesize silver nanoparticles (Balaji et al. 2009). It was suggested that proteins, organic acids and polysaccharides released by *C. cladosporioides* were responsible for formation of spherical crystalline silver nanoparticles. Kathiresan et al. (2009) have shown that when the culture filtrate of *Penicillium fellutanum* was incubated with silver ions and maintained under dark conditions, spherical silver nanoparticles could be produced. Penicillium sp. J3 isolated from soil was able to produce silver nanoparticles. The bioreduction of silver ions occurred on the surface of the cells and proteins might have critical role in formation and stabilization of the synthesized nanoparticles (Maliszewska et al. 2009).

Sanghi and Verma (2009) investigated the ability of *Coriolus versicolor* in formation of monodisperse spherical silver nanoparticles. The time taken for production of silver nanoparticles was reduced from 72 to 1 h under alkaline conditions (pH 10). It was indicated that alkaline conditions might be involved in bioreduction of silver ions, water hydrolysis and interaction with protein functionalities. Findings of this study have demonstrated that glucose was necessary for the reduction of silver nanoparticles, and S-H of the protein played an important role in the bioreduction.

3.2.6.3 Algae

Cyanobacteria and eukaryotic alga genera such as *Lyngbya majuscule*, *Spirulina subsalsa*, *Rhizoclonium heiroglyphicum*, *Chlorella vulgaris*, *Cladophora prolifera*, *Padina pavonica*, *Spirulina platensis*, and *Sargassum fluitans* can be used as cost-effective means for biorecovery of gold out of the aqueous solutions, as well as the formation of gold nanoparticles (Chakraborty et al. 2009; Lengke et al. 2006a, b; Niu and Volesky 2000). Marine algae like *Chaetoceros calcitrans*, *Chlorella salina*, *Isochrysis galbana* and *Tetraselmis gracilis* can also be used for reduction of silver ions and thereby synthesis of silver nanoparticles. Marine cyanobacterium, *Oscillatoria willei* NTDM01 has been used for synthesis of silver nanoparticles (~100–200 nm). The color of silver nitrate solution incubated with washed marine cyanobacteria was changed to yellow from 72 h onwards, indicating the formation of silver nanoparticles. When *Spirulina platensis* biomass was exposed to 10^{-3} M aqueous $AgNO_3$, extracellular formation of spherical silver nanoparticles (~7–16 nm) was resulted in 120 h at 37 °C at pH 5.6 (Govindaraju et al. 2008). Proteins might be responsible for reduction and stabilization of the nanoparticles. In the case of *C. vulgaris*, the proteins in the extract had dual function of Ag^+ ion reduction, and shape controlled synthesis of nanoparticles. The silvernano plates were obtained at room temperature. Reduction of Ag^+ ions was done by hydroxyl groups in Tyr residues and carboxyl groups in Asp/Glu residues. This was responsible for the anisotropic growth of silver nano plates which yielded rod-like particles with a mean length of 44 nm and width of 16–24 nm. In one study, a sustained synthesis of colloidal gold (~9 nm) using *Klebsormidium flaccidum* green algae was reported. According to the findings, ca. 16 wt.% of gold was cellular Au and ca. 80 % of it was metallic Au content, indicating an effective intracellular reduction process (Dahoumane et al. 2012).

3.2.6.4 Plants and Phytochemicals

Green synthesis of metal and metal oxide nanoparticles by plants and phytochemicals is mainly advantageous in terms of environmental friendliness. But, major drawbacks associated with this green process are longer reaction times, tedious purification steps, greater sizes of all nanoparticles and poor understanding of the underlying mechanisms. Optimization of this green method is critical to for fast and clean synthesis of nanoparticles with desired sizes and morphologies. Several studies reported the bioreduction of metallic ions using various plants and phytochemicals in order to synthesize metallic nanoparticles. For instance, *Beta vulgaris* (pulp extract) (Castro et al. 2011), *Nycanthes arbortristis* (flower extract) (Das et al. 2011), *Mangifera indica* (leaf extract) (Phillip 2010), *Ficus carica* (leaf and bark extracts) (Singh and Bhakat 2012), *Sphearanthus amaranthoids* (leaf extract) (Nellore et al. 2012), *Putranjiva roxburghii* (leaf extract) (Badole and Dighe 2012), *Terminalia catappa* (leaf extract) (Ankamwar 2010) and *Stevia rebaudiana* (leaf extract) (Mishra et al. 2010) were used for synthesizing metallic nanoparticles. Moreover, Song and Kim (2009) have elucidated that *Pinus desiflora*, *Diospyros kaki*, *Ginko biloba*, *Magnolia kobus* and *Platanus orientalis* leaves broth synthesized stable silver nanoparticles with average particle size ranging from 15 to 500 nm, extracellularly. In the case of *M. kobus* and *D. kaki* leaf broth, synthesis rate and final conversion to silver nanoparticles became faster, when reaction temperature increased. But the average particle sizes produced by *D. kaki* leaf broth decreased from 50 to 16 nm, when temperature was increased from 25 to 95 °C. They also illustrated that only 11 min was required for more than 90 % conversion at the reaction temperature of 95 °C using *M. kobus* leaf broth (Song and Kim 2009). Vilchis-Nestor et al. (2008) used *Camellia sinensis* extract to produce gold nanoparticles and silver nanostructures in aqueous solution at ambient conditions. They also investigated control of size, morphology, and optical properties of the nanostructures and reported initial concentrations of metal ions and tea extract as controlling factors. It was investigated that when the amount of *C. sinensis* extract was increased, the resulted nanoparticles were slightly bigger and more spherical. Authors of this study believed that phenolic acid-type biomolecules present in *C. sinensis* extract were responsible for production and stabilization of silver and gold nanoparticles. Caffeine and theophylline present in tea extracts might be responsible for catalysis and synthesis of nanoparticles. In another study, black tea leaf extracts were used in production of gold and silver nanoparticles (Begum et al. 2009). The nanoparticles were stable and had different shapes, such as spheres, trapezoids, prisms, and rods. Findings of this study demonstrated that polyphenols and flavonoids were responsible for synthesis of nanoparticles. Moreover, tea leaf extracts in 1-methyl-2-pyrrolidinone solution were used for fabrication of 20 nm gold nanoparticles (Afzal et al. 2009). These nanoparticles were incorporated in 1-methyl-2-pyrrolidinone solution of polyaniline emeraldine base to cast the nanocomposite films. In addition, green method for synthesizing gold nanoparticles was reported by mixing the Au(III) ion-dissolved rice wine and soda at pH 6.5 at a slightly elevated temperature (25–55 °C) in the absence of extra protective agents (Wu and Chen 2007). Rice wine was used as a solvent and a reducing agent; soda not only functioned as a protective agent but also played the role of base catalyst. The resultant solution was quite stable and no precipitation occurred even after several months.

Sathishkumar et al. (2009a) investigated the synthesis of palladium nanoparticles through reduction process using *Cinnamomum zeylanicum* bark extract. As a result, nano-crystalline palladium particles (~15–20 nm) were synthesized. It was demonstrated that reaction conditions such as pH, temperature, and biomaterial dosage had no major effects on the shape and size of produced nanoparticles. One-pot biogenic fabrication of palladium nanoparticles (~3.2–6.0 nm) was also carried out by a simple procedure using broth of *Cinnamomum camphora* leaf without extra surfactant, capping agent and/or template (Yang et al. 2010). The size of palladium nanoparticles could be easily controlled by variation of the initial concentration of Pd (II) ions. In another study, nano-crystalline palladium particles (~10–15 nm) were synthesized using *Curcuma longa* tuber extract as biomaterial. Temperature and pH had no major effect on size and shape of the nanoparticles. It was found that the zeta potential of formed palladium nanoparticles was negative and it was increased by increasing the pH (Sathishkumar et al. 2009c). It was also reported that palladium nanoparticles could be synthesized by using coffee and tea extract. The produced nanoparticles were in the size range of 20–60 nm and crystallized in face centered cubic symmetry (Nadagouda and Varma 2008b). It was reported that *Gardenia jasminoides* Ellis' aqueous crude extract could be used for bioreduction of palladium chloride. Identified antioxidants, including geniposide, chlorogenic acid, crocins and crocetin were reducing and stabilizing agents for synthesizing palladium nanoparticles (~3–5 nm) in aqueous crude extract. The particle size and dispersity of nanoparticles were temperature dependent, and the best dispersity was revealed at 70 °C (Jia et al. 2009). Palladium nanoparticles were synthesized under moderate pH and room temperature using *Solanum trilobatum* conjugated with lipoic acid (S-PdNP-LA) and vitamins (S-PdNP-Vitamin-LA). S-PdNP were polydisperse and of different morphologies ranging from 60 to 70 nm (S-PdNP), 65–80 nm (S-PdNP-LA), and 75–100 nm (S-PdNP-Vitamin-LA) in size (Kanchana et al. 2010). Moreover, palladium nanoparticles (~15 nm) were synthesized by using a soybean (*Glycine max*) leaf extract-mediated biosynthesis process. Protein-rich soybean leaf extract acted as an effective reducing agent for palladium ions (Petla et al. 2012).

Platinum nanoparticles (~2–12 nm) could be synthesized using the leaf extract of *Diopyros kaki* (as a reducing agent). It was reported that more than 90 % of the platinum ions were converted into nanoparticles with a 10 % leaf biomass concentration at 95 °C (Song et al. 2010). The sizes of the produced nanoparticles were dependent on the reaction temperature and concentrations of the leaf broth and $PtCl_6^{2-}$. The leaf extract of Ocimum sanctum was used as a reducing agent for the synthesis of platinum nanoparticles (~23 nm). Fourier-transform infrared (FTIR) spectroscopy revealed that the compounds such as ascorbic acid, gallic acid, terpenoids, certain proteins and amino acids act as reducing agents for platinum ions reduction. It was reported that the reduced platinum showed similar hydrogen evolution potential and catalytic activity like pure platinum using linear scan voltammetry (Soundarrajan et al. 2012). In another study, one-pot synthesis of platinum and palladium nanoparticles using lignin isolated from red pine (*Pinus resinosa*) was reported. Spherical nanoparticles (~16–20 nm) were observed in the case of palladium, and smaller ones of not so well defined shapes for platinum. These nanoparticles showed good catalytic activity in the reduction reaction (Coccia et al. 2012).

In_2O_3 nanoparticles (~5–50 nm) were produced by using indium acetylacetonate and *Aloe vera* plant extracted solution (Maensiri et al. 2008). The nanoparticles were formed after calcinations of the dried precursor of indium oxide in air at 400–600 °C. The morphology and size of indium oxide nanoparticles were affected by the temperature of calcination. Moreover, copper nanoparticles were biosynthesized using Magnolia leaf extract. When aqueous solutions of $CuSO_4 \bullet 5H_2O$ treated with the leaf extract, stable copper nanoparticles (~40–100 nm) were formed. The produced nanoparticles showed higher antibacterial activity against *E. coli* cells (Lee et al. 2011). In another study, extracellular production of copper nanoparticles was carried out using stem latex of a medicinally important plant, *Euphorbia nivulia*. The produced nanoparticles were stabilized and subsequently capped by peptides and terpenoids present within the latex. The copper nanoparticles were toxic to adenocarcinomic human alveolar basal epithelial cells (A549 cells) in a dose dependent manner. It was concluded that the non-toxic aqueous formulation of latex capped copper nanoparticles could be directly used for administration/in vivo delivery of nanoparticles for cancer therapy (Valodkar et al. 2011). Furthermore, Cu_2O nanoparticles were biologically synthesized by reduction of Barfoed's solution, using agriculture wastes of *Arachis hypogaea* L. leaf extracts containing reducing sugars. The aldehyde group present in reducing sugar plays an important role in the formation of cuprous oxide nanoparticles in the solution. It was demonstrated that the produced cuprous oxide nanoparticles had antibacterial effects on *E. coli* (Ramesh 2011). Furthermore, the synthesis of hexagonal wurtzite ZnO nanoparticles by Zn-hyper-accumulator (*Sedum alfredii* Hance) plants was reported. The formed nanoparticles were agglomerated, and single ZnO nanoparticles were pseudo-spherical in shape with a mean size of 53.7 nm (Qu et al. 2011a). In another study, crystalline zinc oxide nanoparticles (~72.5 nm) were biologically synthesized using *Physalis alkekengi* L. The TEM images demonstrated that the nanoparticles were polydispersed and not uniformly distributed (Qu et al. 2011b). Moreover, highly stable and spherical zinc oxide nanoparticles (~25–40 nm) were produced using zinc nitrate as the substrate and *Aloe barbadensis* Miller leaf extract as the biocatalyst. Consequently, greater than 95 % conversion to nanoparticles was achieved using concentrations more than 25 % of *A. barbadensis* leaf broth. The produced nanoparticles were polydispersed (Sangeetha et al. 2011). Green synthesis of ZnO nanoparticles (~30–35 nm) by zinc nitrate and utilizing the leaf extract of *Calotropis gigantea*has been reported. The SEM image showed relatively spherical shape nanoparticles (Vidya et al. 2013).

A green approach for synthesis of titanium dioxide nanoparticles from titanium isopropoxide solution using *N. arbortristis* leaves extract was reported. SEM analysis demonstrated that the average size was from 100 to 150 nm, and the shapes were spherical and uniformed (Sundrarajan and Gowri 2011). Furthermore, green synthesis of TiO_2 nanoparticles (~25–100 nm) by using 0.3 % aqueous extract prepared from latex of *Jatropha curcas* L. was reported. These nanoparticles were characterized by X-ray diffraction (XRD), Selected Area Electron Diffraction (SAED), Transmission Electron Microscopy (TEM), Energy Dispersive Analysis of

X-rays (EDAX) and Fourier Transform Infrared Spectroscopy (FTIR). FTIR were performed to find the role of curcain (an enzyme), cyclic peptides namely curcacycline A (an octapeptide) and curcacycline B (a nonapeptide) as a possible reducing and capping agent, present in the latex of *J. curcas* L. The produced nanoparticles were mostly spherical in shape (Hudlikar et al. 2012). In one study, *Eclipta prostrata* leaf extract was used for green synthesis of titanium dioxide nanoparticles (~36–68 nm) (Rajakumar et al. 2012). FTIR peak implicated the role of carboxyl group O-H stretching amine N-H stretch in the formation of titanium dioxide nanoparticles. XRD characterized the crystallographic plane of rutile phase (iv) Atomic Force Microscopy (AFM) showed uneven surface morphology which indicates the presence of both individual and agglomerated nanoparticles. The surface of synthesized nanoparticles was characterized using Field Emission Scanning Electron Microscopy (FESEM). This analysis showed shape of spherical clusters, quite polydisperse (Rajakumar et al. 2012).

3.3 Spectroscopic Characterization of Nanoparticles

Most of the nanoparticle characterization techniques can be classified in two broad categories (Herrera and Sakulchaicharoen 2009).

1. Local probe techniques
    - (i) Scanning Electron Microscopy (SEM)
    - (ii) Transmission Electronic Microscopy (TEM)
    - (iii) Scanning Tunneling Microscopy (STM)
    - (iv) Atomic Force Microscopy (AFM)
2. Bulk sensitive techniques
    - (i) Optical absorption spectroscopy
    - (ii) Fourier Transform Infra-red (FT -IR)spectroscopy spectroscopy
    - (iii) Electron Spin Resonance (ESR) Spectroscopy
    - (iv) Raman scattering
    - (v) X-ray based techniques

This contribution presents review of recent trends in nanoparticle characterization using the following two spectroscopic techniques only.

(i) UV-visible spectroscopy
(ii) FT-IR spectroscopy

A brief account of the Electron Magnetic Resonance (EMR) characterization of nanoparticles has been separately published (Shukla 2015). However detailed account of different characterization techniques is beyond the scope of this article and can be found elsewhere (Lungu et al. 2015).

3.3.1 Optical Properties of Nanoparticles and Surface Plasmon Resonance

Surface Plasmon Resonance is responsible for unique optical properties of metal nanoparticles. Interaction between the incident electromagnetic radiation and surface electrons of metal nanoparticles is responsible for the surface plasmon resonance. Surface plasmons are generated by the coupling between the oscillation modes of incident electromagnetic radiation and the oscillations of conduction electrons (Collective oscillations of conduction electrons in resonance with electromagnetic field). Field is enhanced at the interface and the effect is more significant with decreasing size though the other parameters like particle shape, composition and surrounding medium also play their role. Surface Plasmon experiments are mostly performed using nanoparticles of noble metals like silver, gold and copper as their Plasmon absorption bands have well defined values in the visible region of the electromagnetic spectrum (Upstone 2000). Gold and silver nanoparticles of size 5–50 nm show strong absorption band around 520–560 nm and 390–420 nm wavelength range respectively (Henglein 1999; Henglein and Meisel 1998). Composition dependence provides another way to tailor the properties using a combination (nanoalloys) say silver-gold for example. Silver-gold combination is interesting because of one more reason other than well defined surface Plasmon resonance bands. Both metals form face centered cubic crystals with similar lattice constants. Therefore alloy of any composition can be formed at bulk as well as nano level (Link et al. 1999). Absorption band position also depends on the shape of nanoparticles. When spherical nanoparticles are elongated (nanorods) then two different resonance modes are observed namely longitudinal surface Plasmon absorption and transverse surface plasmon absorption depending on the orientation with respect to the direction of incident electric field.

3.3.2 UV-Visible Spectroscopic Characterization

UV-visible absorption spectroscopy plays very important role to investigate the optical properties of nanoparticles. Quantitative formation can be monitored and size of nanoparticles can be studied with the help of this technique. It is basically study of response to electromagnetic waves in the wavelength range 190–700 nm by the sample (Upstone 2000). Now we cite some examples from recent literature to highlight the applications of UV-visible spectroscopy in nanoparticle characterization.

Awaad and Salem (2012) have reported the green synthesis of silver nanoparticles by mulberry leaves extract. They have used UV-visible absorption spectrum in the wavelength range 200–800 nm to confirm the formation and stability of silver nanoparticles synthesized by green synthesis. They monitored the reduction of pure Ag^+ ion to Ag^0 nanoparticles at regular interval of time and could obtain a peak after 30 min at 425 nm. There was no change in the wavelength in the peak position with

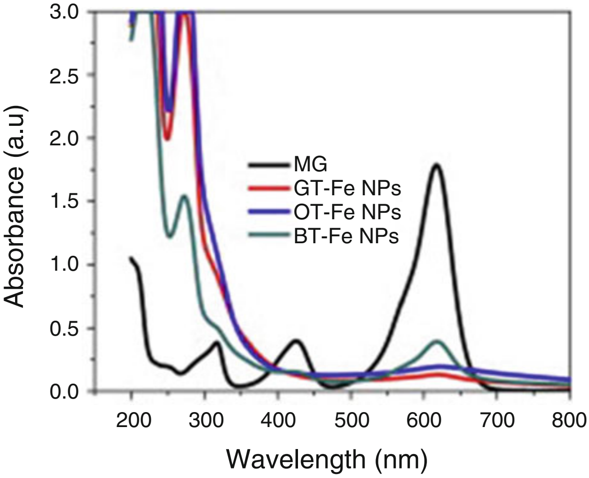

Fig. 3.1 UV-visible absorption spectrum showing the degradation of Malachite Green using different types of tea extracts. It may be noticed that Fe nanoparticles synthesized by green tea extracts are best for degrading Malachite green. GT, OT and BT stands for *green*, oolong and black teas respectively (Reproduced with permission)

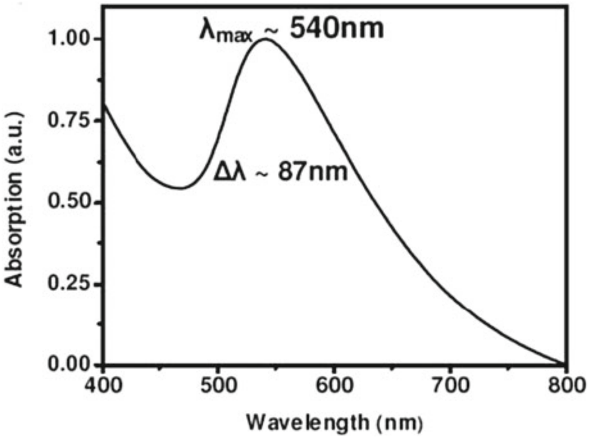

Fig. 3.2 UV-visible absorption spectrum of gold nanoparticles synthesized from *Allium cepa* extract. Strong resonance which arises due to the excitation of surface plasmon resonance at 540 nm is clearly noticed (Reproduced with permission)

time onwards and it could be concluded that after 60 min there was no increase in the number and size of the nanoparticles, the reason being depletion of Ag^+ ions in the extract.

Synthesis of iron nanoparticles using green method based on tea extracts, including green, oolong and black teas is reported by Huang et al. (2014). With the help of UV-visible experiments they have been able to state that such iron nanoparticles synthesized from tea extracts are best for degrading of malachite green (Fig. 3.1).

Parida et al. (2011) have reported UV-visible absorption study of gold nanoparticles synthesized from *Allium cepa* extract. A strong resonance at 540 nm is clearly seen and arises due to the excitation of surface plasmon resonance in the gold nanoparticles (Fig. 3.2).

Maddinedi et al. (2015c) have confirmed the formation of gold nanoparticles using a natural enzyme Diatase using UV-visible spectrum with a characteristic

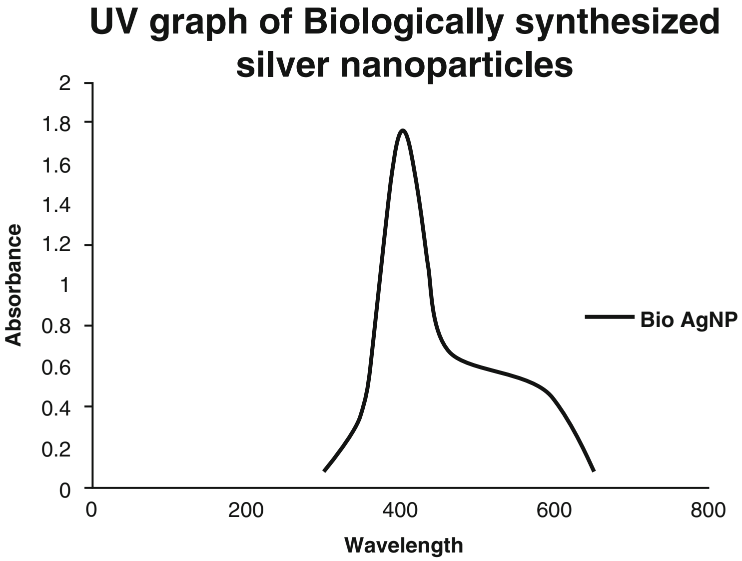

Fig. 3.3 UV-visible spectrum of chemically synthesized silver nanoparticles (Reproduced with permission)

surface plasmon resonance band at 530 nm. The size of the diastase-stabilized gold nanoparticles is reported to be controlled by changing the quantity of diastase.

Banerjee et al. (2014) have reported UV-visible characterization of silver nanoparticles synthesized by green route from three Indian medicinal plants, *M. balbisiana* (banana), *A. indica* (neem) and *O.tenuiflorum* (black tulsi). Spectra were recorded with time and the absorption band was found in the range of 425–475 nm due to surface Plasmon resonance. They could infer that most rapid bioreduction was achieved using banana leaf extract as reducing agent followed by tulsi and neem leaf extracts. It was also found from UV-visible analysis that formation of silver nanoparticles occurred rapidly within the first 15 min only and the nanoparticles remained stable even after 24 h of completion of reaction.

Green synthesis and UV-visible characterization of silver nanoparticles using fenugreek seed extract have been reported by Angelina et al. (2013). They have recorded spectra periodically after a day and could find from the broadening and red shift that particle size increases with time. Nandita et al. have analyzed the nano-silver and protein (bovine serum albumin) interaction using this technique (Nandita et al. 2016).

Green synthesis and characterization of silver nanoparticles synthesized from *Morus nigra* leaves extract has been reported by Kumar et al. (2013). They could monitor reduction of Ag^+ ions by recording UV-Visible spectrum. From the surface plasmon band position, they were able to distinguish between chemically synthesized silver nanoparticls (Fig. 3.3) and biologically synthesized silver nanoparticles (Fig. 3.4). Moreover they were able to estimate the shape of nanoparticles.

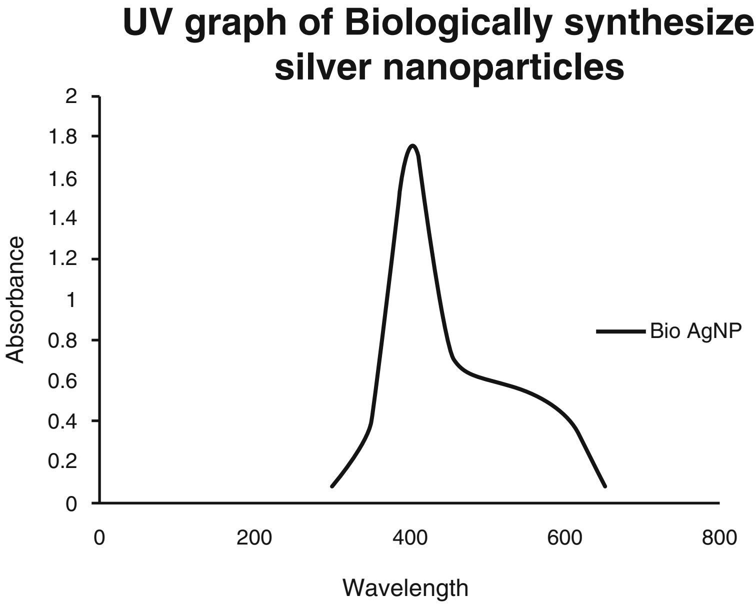

Fig. 3.4 UV-visible spectrum of biologically synthesized silver nanoparticles (Reproduced with permission)

Green synthesis and characterization of silver nanoparticles synthesized by aqueous leaf extracts of *Cardiospermum helicacabum* leaves has been reported by Mitra et al. (2012). UV visible spectra were recorded for different concentration, time and temperature. It was concluded that high Plasmon resonance could be obtained for 20 % concentration.

Pattanayak and Nayak (2013) have reported green synthesis and characterization of iron nanoparticles from the leaf extract of *Azadirachta indica* (neem). In their study they found appreciable surface plasmon resonance in 216–265 nm range of wavelength.

UV-visible spectrum of synthesized silver nanoparticles using *S. xanthocarpum*-berry extract as a reducing and capping agent has been reported by Amin et al. (2012). They found that high pH value, temperature and molar ratio of *S. xanthocarpum* extract to $AgNO_3$ could accelerate the reduction rate of Ag^+ and affect the Ag nanoparticle size.

Monitoring of synthesis of colloidal sliver nanoparticles prepared from different plant leaves extract using UV-Visible spectroscopy has been reported by Okafor et al. (2013). The UV-Visible spectrum showed a peak between 417 and 425 nm corresponding to the plasmon absorbance of the silver nanoparticles. They could conclude that silver nanoparticles synthesized by green methods at low concentrations are not cytotoxic for human healthy cells but inhibit bacteria growth. Authors emphasized the need to carry further investigations to determine the minimum inhibitory concentration of silver nanoparticles for bacterial growth, and cytotoxic effects of biosynthesized silver nanoparticles on cancerous and other healthy cells.

Senapati et al. (2013) have reported green synthesis and characterization of ZnS nanoparticles using glucose as capping agent. In their UV-visible absorption study they have found strong absorption below 300 nm and with the help of blue shift obtained with respect to the bulk ZnS they have predicted quantum confinement in the sample. Band gap energy has also been calculated and they have been able to estimate the size of nanoparticles with the help of blue shift.

3.3.3 FT-IR Spectroscopy and Nanoparticle Characterization

FT-IR spectroscopy is applied to find out information about the different functional groups from the peak positions in the spectrum. Information about capping and stabilization of the nanoparticles may also be inferred from this analysis. Now we cite some examples from recent literature to highlight the applications of FT-IR spectroscopy in nanoparticle characterization.

FTIR analysis carried out to characterize the silver nanoparticles obtained from three Indian medicinal plants, *M. balbisiana* (banana), *A. indica* (neem) and *O. tenuiflorum* (black tulsi) has been reported by Banerjee et al. (2014). In all three cases, prominent bands of absorbance were observed at around 1025, 1074, 1320, 1381, 1610 and 2263 cm^{-1}. They have concluded that observed peaks denote -C-OC-, ether linkages, -C-O-, germinal methyls, -C=C- groups or from aromatic rings and alkyne bonds, respectively. They have suggested that these bands may be responsible for efficient capping and stabilization of obtained silver nanoparticles.

Awaad and Salem (2012) have reported the FT-IR study of mulberry leaves extract to investigate the functional groups. They have found that the carboxyl (-C=O), hydroxyl (-OH) and amine (N-H) groups of mulberry leaves extract are mainly involved in reduction of Ag^+ to Ag nanoparticles.

Shahwan et al. (2011) have reported FT-IR analysis of iron nanoparticles synthesized by green tea before and after degradation reactions with methylene blue and methyl orange dyes. Spectral features after contact with methylene blue solution were obtained at 2925 cm^{-1} and 2818 cm^{-1} attributable to the stretching vibration of C–H in the methyl groups, originating from methylene blue and/or its degradation products (Imamura et al. 2002). Spectral features after contact with methyl orange solution appeared at 2927 cm^{-1} and was attributed to asymmetric $-CH_3$ vibrations. Additional peaks were assigned to –C–S– stretching vibrations (Pashetti et al. 2010).

FT-IR analysis of silver nanoparticles bio-synthesized using *Potentilla fulgens* extract has been reported recently to investigate the possible reducing functional groups present in the P. fulgens root extract (Mittal et al. 2015). The FT-IR spectrum of nanoparticles showed the involvement of O-H stretching, involvement of C=N in plane vibrations of amino acids, corresponding to amides I, II and III, aromatic rings and ether linkages. From the observed peaks authors have suggested the presence of flavonoid, phenolicsand terpenoids capped on nanoparticles.

Sadeghi and Gholamhoseinpoor (2015) have found the FT-IR spectra (Fig. 3.5) of the *Z. tenuior* (Zt) leaf extract before and after bioreduction very different. They could conclude from the structural changes that the reduction and stabilization of silver nanoparticles proceeds via the coordination between nitrogen of the amide group and silver ions. Proteins could possibly form a layer capping of silver nanoparticles to prevent agglomeration and thereby stabilize the medium.

In another report, Sadeghi et al. (2015) have reported FT-IR result of silver nanoparticles synthesized using seed aqueous extract of *Pistacia atlantica* and found that the extracts containing OH as a functional group act in capping the nanoparticles.

Molecular interactions of silver nanoparticles obtained with polyethylene glycol suspension and gluconic acid products by reduction of sugar compound were confirmed by FT-IR spectra by Shameli et al. (2012). They have suggested that hydroxyl group of polyethylene glycol as capping agent can make a cover on the surface of silver nanoparticles. This is possible because the surface of silver nanoparticles is positively charged.

The leaf biomass before bioreduction, the biomass residue after bioreduction and the resulting palladium nanoparticles synthesized by broth of *Cinnamomum camphora* leaf were analyzed by FT-IR by Yang et al. (2010). Information regarding chemical transformation of the functional groups involved in reduction of palladium ions could be obtained and it was inferred that the polyols such as flavones, terpenoids, and polysaccharides in the broth played a critical role with dominant role of the water soluble fractions in reduction of Pd(II) ions.

Senapati et al. (2013) have reported FT-IR characterization of ZnS nanoparticles synthesized using glucose as capping agent. They have been able to identify the presence of –CO and –OH groups of glucose which have strong ability to bind metals.

3.4 Applications and Challenges

Nanoparticles have found their applications in diverse fields. Silver nanoparticles are popular for their, catalytic, antibacterial and microorganism elimination applications (Okafor et al. 2013; Awaad and Salem 2012). Other applications of silver nanoparticles include their use as selective coating material for solar energy absorption (Bonsak et al. 2011) and as optical receptors for biolabeling (McFarland and van Duyne 2003). Gold nanoparticles have found their application as bio censors in living cells and can lead to cancer diagnostics in addition to their other applications (El-Sayed et al. 2005). Titanium dioxide is a material of great significance in many fields, e.g., photo catalysis, solar cell devices, gas sensors, and biomaterials. The non-toxic and biocompatible properties of TiO_2 find its applications in biomedical sciences such as bone tissue engineering as well as in pharmaceutical industries.

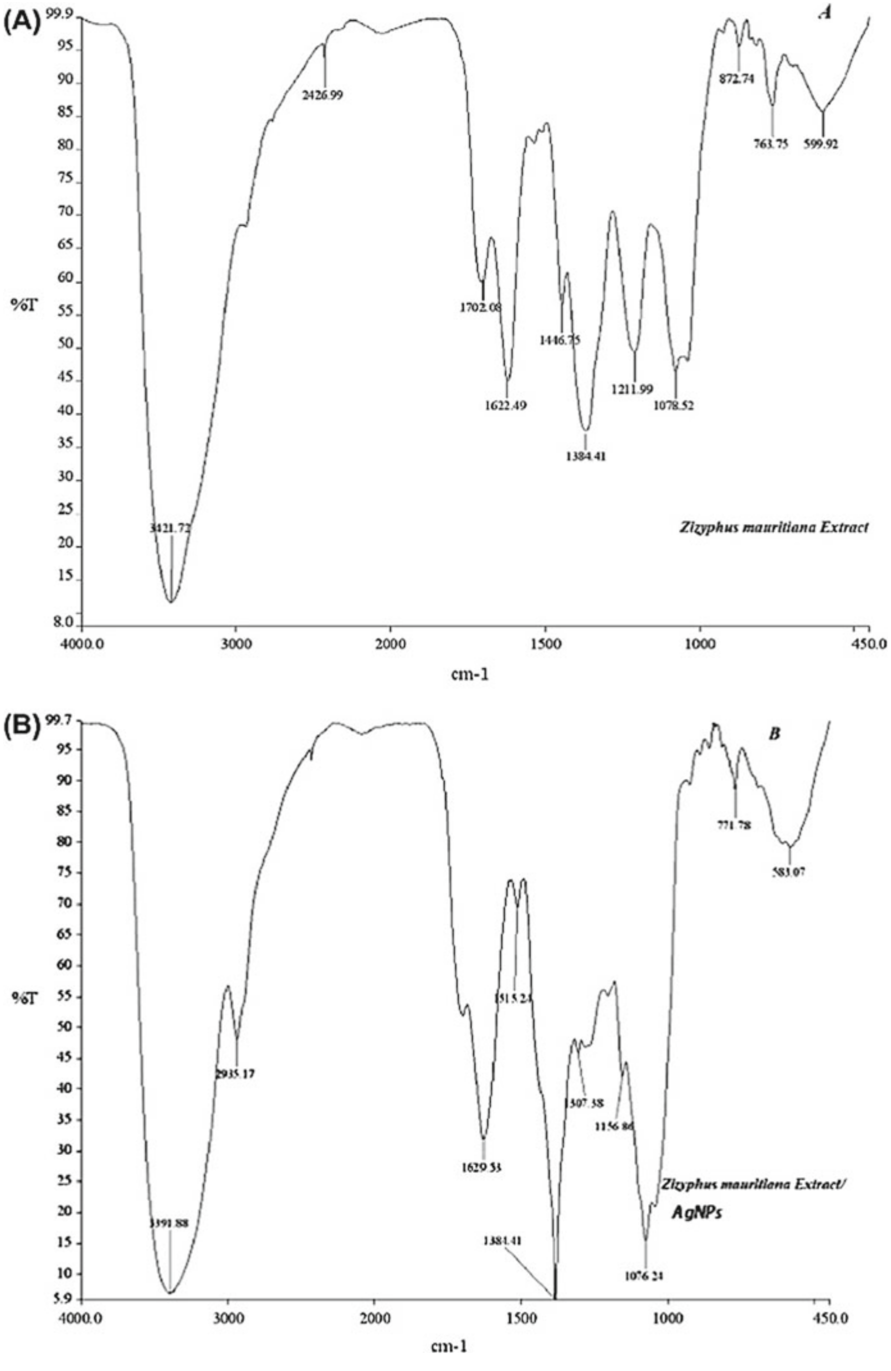

Fig. 3.5 FT-IR spectra of *Ziziphora tenuior* (Zt) powder (**a**) before and (**b**) after reaction. Possibly proteins could form a layer capping of silver nanoparticles to prevent agglomeration and stabilize the medium (Reproduced with permission)

Titanium dioxide catalysts have been confirmed to be excellent and efficient photocatalysts for the degradation and inhibition of numerous toxic environmental contaminants. Different applications of TiO_2 include air and water cleaning and surface cleaning (Malarkodi et al. 2013). II-VI class inorganic semiconductor nanomaterials like CdS, ZnS, CdSe have found important applications in optoelectronic devices (Senapati et al. 2013). Among these several applications it will be relevant to cite a few from the field of water purification technology which is no doubt on the top priority in present days. The technologies in practice for the treatment of waste water include ion-exchange, reverse osmosis, ultra-filtration, ozonization, oxidation and adsorption. High operation cost, relatively low efficiency and generation of toxic products are the prime concerns of these technologies which have led to the research for new alternatives. Nanomaterials have been explored to provide the alternative approaches in this area (Das and Mandal 2015). Crane and Scott (2012) have pointed it out that due to its capability for removal of different chemicals, nanoscale iron is supposed to serve as a tool to remove contamination from water and soil. Water purification technique for the treatment of dye bearing contaminated water through cost-effective and eco-friendly nanocomposite based method is reported by Das et al. (2013). They have reported a process to prepare silver – silica nanocomposite for treatment of waste water. However the need to examine the reversible nature of remediation in water using nanoscale particles seeks further concentrated efforts to validate the technology and open up/establish the new dimensions in the area of water purification.

3.5 Conclusion

In this chapter, we have discussed green methods for nanoparticle synthesis and their characterization through UV-visible and FT-IR spectroscopic techniques. We have also highlighted their applications in water purification while mentioning some other reports on their applications in other fields. Green methods eliminate the need to use harsh, toxic and expensive chemicals. Actually there are several investigations carried out at research laboratories in small scale but unfortunately there are few reports on industrial-scale fabrication of nanoparticles using green methods. Optimization of the reaction conditions and extraction and purification of the produced nanoparticles and separation according to size and shape are important aspects for green synthesis of nanoparticles. Therefore it is the need of the hour to pay attention on scaling up the processes of the preparation of nanoparticles.

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Chapter 4
Nanotechnology to Remove Contaminants

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Abstract Emerging contaminants will be a major challenge for human health and environment since their concentrations are increasing. Contaminants occur in air, soil and aquatic media, then finally end up in drinking water. Contaminants cause many health issues to living organisms, by disruption of endocrine systems and feminization of male fish, for instance. Therefore, prevention of contaminant release, and cleaning of contaminated media are needed. Many processes, including physical separation, biological treatment and chemical transformation have been set up to remove contaminants. Here we review methods to remove contaminants using nanomaterials, such as nanoparticles, nanotubes, and nanostructured membranes. New processes based on nanostructured materials such as TiO_2 nanowires or nanofiltration membrane can achieve up to 95 % removal of contaminants.

Keywords Nanotechnology • Remediation • Sensors • Agriculture • Environment

4.1 Introduction

Emerging contaminants are a number of polluting compounds, which are of emerging public interest due to potential health or environmental effects. These compounds have been released into environment since their use has commenced (Englert 2007), but they might be beyond the detection limits of analytical methods. In the past 20 years, by developing sophisticated analytical instrument, researchers have detected them in different environmental compartment, including water, air, soil and sediments.

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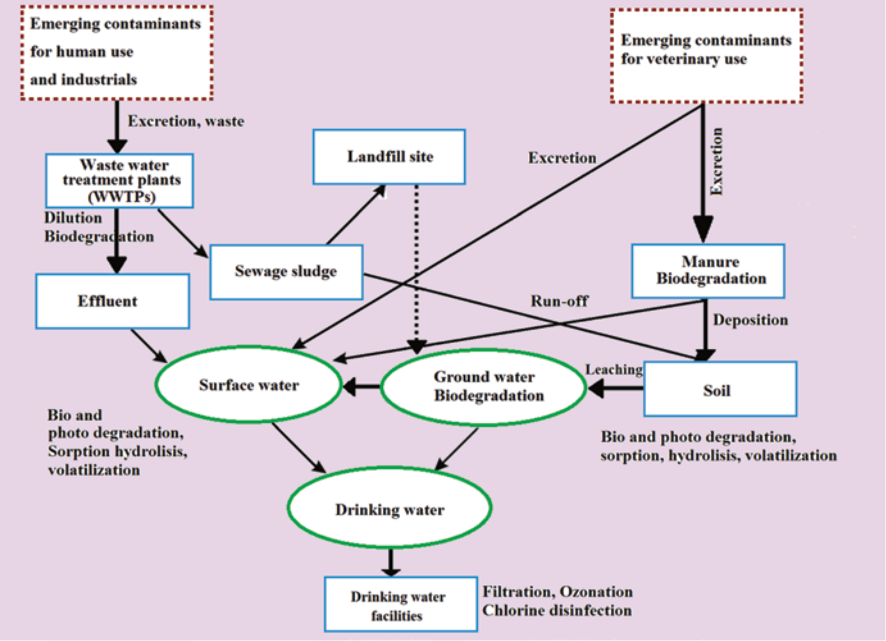

Fig. 4.1 Distribution of emerging contaminants in the environment. Subsequent to human, veterinary and industrial use and then releasing into wastewater, emerging contaminants can easily find their ways into soil, ground water, surface water and finally drinking water

The possible routes for transport of emerging contaminants from point of use to drinking water have been illustrated in Fig. 4.1. In the case of pharmaceutically active compounds, veterinary drugs find their ways into soil when manure is used on agricultural field. Later, they can go to groundwater or surface water through leaching or run-off from livestock slurries, respectively. Also, excess human pharmaceuticals and other chemical compounds in the customer products end up in wastewater treatment plants and afterwards, they can enter aquatic media through effluent or soil via biosolids (Farre et al. 2008). It is noteworthy that compounds with higher volatility can go to air form soil or water.

Until date, there is limited regulatory status for the majority of emerging contaminants and their metabolites (Deblonde et al. 2011) however their effects on ecosystem and human health is becoming more obvious as a result of recent research works. For example, the increased number of female fish in some aquatic media is attributed to steroid hormones that find their way into rivers from municipal wastewater treatment systems (Spina et al. 2013). Also, there are reports on the relation of polybrominated diphenyl ethers and cancer proliferation (Siddiqi et al. 2003). Until now, three lists for emerging contaminants are published by the United States Environmental Protection Agency and the draft of fourth list is prepared. In Table 4.1, different classes of emerging contaminants with related examples have been presented.

To prevent adverse effects of emerging contaminants, capability of their efficient removal from different environmental compartments is of high importance. Different

Table 4.1 Classification of different emerging contaminants. Since 1998, US Environmental Protection Agency updated the list of emerging contaminants four times and the below list is in accordance to the draft of latest list prepared in 2015

Class of emerging contaminants	Examples	Definition
Antibiotics	Tetracycline	Medications that fight bacterial infections, inhibiting or stopping bacterial growth
	Erythromycin	
Disinfectants	Alcohols	A chemical agent used on non-living surfaces to destroy, neutralize, or inhibit the growth of disease-causing microorganisms
	Aldehydes	
Disinfection by-products	Chloroform	Chemical substances resulting from the interaction of organic matter in water with disinfection agents, such as chlorine
	Nitrosodimethylamine	
Drugs of abuse	Amphetamine	Drugs are addictive and have long-lasting changes in the brain
	Cocaine	
	Tetrahydrocannabinol	
Hormone mimicking agents	Bisphenol A	Natural or synthetic chemicals that can elicit an estrogenic response
Fire or flame retardants	Polybrominated diphenyl ethers	Any of several materials or coatings that inhibit or resist the spread of fire
	Tetrabromo bisphenol A	
	Tris (2-chloroethyl) phosphate	
Fragrances	Galaxolide	Chemical substances that impart a sweet or pleasant odor
	Polycyclic	
	Macrocyclic musks	
Gasoline additives	Dialkyl ethers	Chemicals that raise gasoline octane number or act as corrosion inhibitors or lubricants
	Methyl-t-butyl ether	
Insect repellants	N, N-diethyl-meta-toluamide	Chemical substances applied to skin or other surfaces to discourage insects from coming in contact with the surface
Poly-aromatic hydrocarbons	Benzo(a) pyrene	A large group of chemical substances usually found in the environment as a result of incomplete burning of carbon-containing materials like fossil fuels, wood, or garbage
	Fluoranthene	
	Naphthalene	
Personal care products	Para-hydroxybenzoate	Chemical substances used in a diverse group of personal items including toiletries and cosmetics
	Benzophenone	
	N,N-diethyltoluamide	
	Methylbenzylidene	

(continued)

Table 4.1 (continued)

Class of emerging contaminants	Examples	Definition
Pesticides or insecticides	Permethrin	Chemical substances or microbiological agents that kill, incapacitate or otherwise prevent pests from causing damage
	Fenitrothion	
	Bacillus Thuringiensis israelensis	
Pharmaceuticals	Carbamazepine	Chemical substances used in the prevention or treatment of physiological conditions
	Acetaminophen	
	Diclofenac	
	Diazepam	
Plasticizers	Dioctyl Phthalate	Chemical additives that increase the plasticity or fluidity of a material
Reproductive hormones	Dihydrotestosterone	A group of chemical substances, usually steroids, whose purpose is to stimulate certain reproductive functions
	Progesterone	
	Estrone	
	Estradiol	
Other hormones	Cholesterol	A large group of fat-soluble organic compounds with a characteristic molecular structure, which includes many natural and synthetic hormones
	Coprostanol	
	Progesterone	
	Diethylstilbestrol	
Solvents	Ethanol	Chemical solutions, other than water, capable of dissolving another substance
	Kerosene	
Surfactants and metabolites	Sodium lauryl sulfate	Chemical substances that affect the surface tension of a liquid
	Alkylphenol ethoxylates	
	Alkylphenols (nonylphenol and octylphenol)	
	Alkylphenol carboxylates	

processes including filtration, adsorption, biodegradation and chemical oxidation are suggested to remove these compounds. However, they need much more research work to satisfy performance and economic requirements. Meanwhile, nanotechnology, with its impacts on scientific and technological breakthroughs, is the most likely tool to revolutionize the purification and remediation processes for contaminated media (Bottero et al. 2006; Chirag 2015; Masciangioli and Zhang 2003; Savage and Diallo 2005; Theron et al. 2008). Nanomaterials exhibit novel physical, chemical and biological properties due to their larger surface area per unit of volume and quantum effects. The potential capabilities of nanotechnology are divided into three classes, including treatment, detection, and prevention (Rickerby and Morrison 2007; Vaseashta et al. 2007). In this chapter, thus, an overview on recent advances in nanotechnology for removing emerging contaminants from different media including water, wastewater and soil is provided. The applications of nanomaterials are critically reviewed based on their structures e.g. nanoparticles, nanotubes, among others and related challenges for their application in full-scale and the research needs for overcoming these challenges are also discussed.

4.1.1 Applications for Water and Wastewater Treatment

At nanoscale, materials show size-dependent properties that are remarkably different from large particles. Several of these scalable properties including fast dissolution, high reactivity, and strong sorption are desirable for water treatment applications. Also, there are several discontinuous properties, such as superparamagnetism, localized surface plasmon resonance, and quantum confinement effect that can be used for specific applications. In Table 4.2, the application of nanomaterials in water treatment processes have been listed. Generally, there are physical separation methods, such as membrane filtration and adsorption system and chemical transformation processes, such as photocatalytic degradation and nanotechnology could enhance all these processes by novel well-structured materials, such as nanofibers, nanotubes, nanoplatelets, nanolayers, among others. In the following sections, the recent research on removal of emerging contaminants using important classes of nanostructured materials have been summarized.

4.1.2 Nanoscale TiO_2

Titanium dioxide (TiO_2), also known as Titania, is a well-known semiconductor with photocatalytic properties. This compound is widely used in advanced oxidation processes for water and air remediation. Nanoscale TiO_2 materials attracted the attention of researchers for their enhanced photocatalytic properties (Dasgupta et al. 2015; Pelaez et al. 2009; Ranjan et al. 2016). As shown in Fig. 4.2, the photocatalytic properties of TiO_2 originated from absorption of ultraviolet light that lead to the formation of charge carriers i.e. hole and electron. The generated holes in the valence band diffuse to the surface of TiO_2 and react with water molecules to form hydroxyl radicals ($OH^\bullet$). On the other hand, oxygen molecule can be reduced by one of generated electrons to a superoxide radical ($O_2^{\bullet-}$) that can be further reduced by another electron or reacts with a hydroperoxyl radical ($HO_2^\bullet$) to form hydrogen peroxide (H_2O_2) (Nakata and Fujishima 2012). Therefore, as a result of light absorption, reactive species, such as hydroxyl radicals and hydrogen peroxide are formed which reacts with contaminants in water and transform them into metabolites.

There are several challenges for commercialization of this process at large scale, such as high operational cost and lack of knowledge on the degradation mechanism. It is obvious that the metabolites of contaminants degradation should be much less toxic than the parent compounds, otherwise, only transforming the contaminants to another unfavorable species will be useless. Measuring the total organic carbon during the reaction is a good criterion to assess the performance of degradation system in transforming the contaminants to non-toxic species. Another challenge for using photooxidation process is the effect of solution chemistry and presence of other constituents in aqueous media, such as sulphate ions that can react with the reactive groups and impede the contaminant degradation.

Table 4.2 Current and potential applications of nanotechnology in water and wastewater treatment (Qu et al. 2013)

Application	Representative nanomaterials	Desirable nanomaterial properties	Enabled technologies	Investigated emerging contaminants
Photocatalysis	Nano-TiO_2	Photocatalytic activity under ultraviolet and visible light range	Photocatalytic reactors	Alachlor
			Solar disinfection systems	Fenitrothion
		Low human toxicity		Trimethoprim
		High stability		
		Low cost		
	Fullerene derivatives	Photocatalytic activity in solar spectrum	Photocatalytic reactors	
		High selectivity	Solar disinfection systems	
Adsorption	Nanoscale metal oxide	High specific surface area	Adsorptive media filters	Aspirin
		Short intraparticle diffusion distance	Slurry reactors	Acetaminophen
				Diclofenac
		More adsorption sites		Arsenate
		Compressible without significant surface area reduction		Polychlorinated biphenyls
				Trichloroethylene
		Easy reuse		
		Superparamagnetic properties		
	Nanofibers with core shell structure	Tailored shell surface chemistry for selective adsorption Reactive core for degradation	Reactive nano-adsorbents	
		Short internal diffusion distance		
	Carbon nanotubes	High specific surface area	Contaminant preconcentration/detection	
		Highly assessable adsorption sites	adsorption of recalcitrant contaminants	
		Tunable surface chemistry		
		Easy reuse		

Membranes processes	Nano-magnetite	Tunable surface chemistry	Forward osmosis	Trimethoprim Norfluoxetine Atorvastatin
		Superparamagnetic properties		
	Nano-TiO_2	Photocatalytic activity	Reactive membranes	*Escherichia coli*
		Hydrophilicity	High performance thin film nanocomposite membranes	
		High chemical stability		
	Nano-zeolites	Molecular sieve	High permeability thin film nanocomposite membranes	
		Hydrophilicity		
	Nano-Ag	Strong and wide-spectrum antimicrobial activity	Anti-biofouling membranes	
		Low toxicity to humans		
	Carbon nanotubes	Antimicrobial activity (unaligned Carbon nanotubes)	Aligned Carbon nanotubes membranes	
		Small diameter		
		Atomic smoothness of inner surface		
		Tunable opening chemistry		
		High mechanical and chemical stability		

(continued)

Table 4.2 (continued)

Application	Representative nanomaterials	Desirable nanomaterial properties	Enabled technologies	Investigated emerging contaminants
Sensing and monitoring	Quantum dots	Broad absorption spectrum, narrow, bright and stable emission which scales with the particle size and chemical component	Optical detection	Aspirin Acetaminophen Diclofenac Ibuprofen
	Noble metal nanoparticles	Enhanced localized surface plasmon resonances	Optical and electrochemical detection	
		High conductivity		
	Dye-doped silica nanoparticles	High sensitivity and stability	Optical detection	
		Rich silica chemistry for easy conjugation		
	Magnetic nanoparticles	Tunable surface chemistry	Sample pre-concentration and purification	
		Superparamagnetism		
	Carbon nanotubes	Large surface area	Electrochemical detection Sample pre-concentration	
		high mechanical strength and chemical stability Excellent electronic properties		
Disinfection and microbial control	Nano-TiO_2	Photocatalytic ROS generation	Point of use to full scale decontamination	*Escherichia coli* *Staphylococcus aureus*
		High chemical stability		
		Low human toxicity and cost		
	Nano-Ag	Strong and wide-spectrum antimicrobial activity	Point of use water disinfection	
		Low toxicity to humans	Anti-biofouling surface	
		Ease of use		
	Carbon nanotubes	Antimicrobial activity	Point of use water disinfection	
		Fiber shape	Anti-biofouling surface	
		Conductivity		

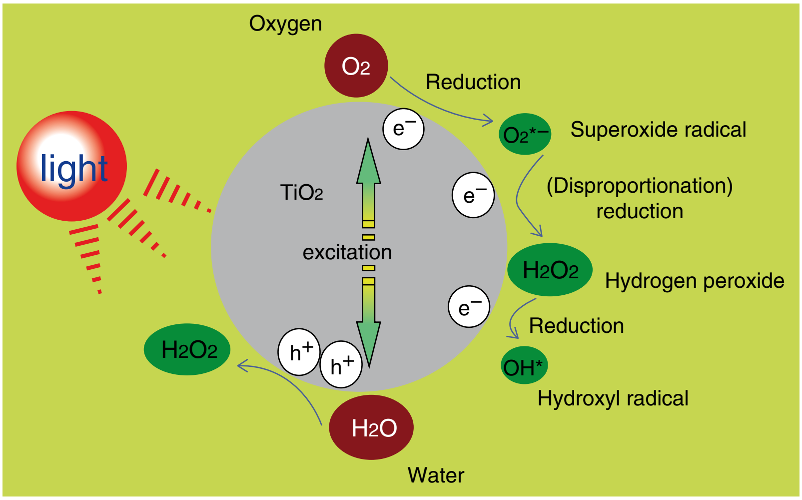

Fig. 4.2 Formation of reactive species as a result of light absorption by TiO_2 photocatalyst. O_2 is reduced by one electron to form superoxide radical ($O_2^{\cdot-}$) that can react with a hydroperoxyl radical ($HO_2^{\cdot}$) to form hydrogen peroxide (H_2O_2). One-electron reduction of H_2O_2 produces hydroxyl radical (OH)

In recent years, researchers have tried to thoroughly investigate the dominants parameters of this process in order to develop an efficient system for removal of all organic contaminants from water. For example, Mahmoodi and Arami immobilized TiO_2 nanoparticles on the walls of their reactor to act as nanophotocatalyst in the presence of ultraviolet irradiation for degradation of two agricultural organic pollutants including Alachlor and Fenitrothion. The results showed that after 180 min of reaction, both compounds degraded and after 240 min complete mineralization was achieved (Mahmoodi and Arami 2010). Hu et al. developed a dense TiO_2 membrane nanowire of 10–20 nm in diameter directly on Ti-atom substrates at 180 °C to prepare a nanophotocatalyst for degradation of trimethoprim, norfluoxetine and atorvastatin as a model pharmaceutical compounds in presence of ultraviolet light irradiation. Their results showed more than 95 % degradation of model compound after 25 min of reaction (Hu et al. 2011).

To investigate the effect of pH and temperature, Liang et al. produced TiO_2 nanobelts with 30–100 nm in width and tens of um in length to use as nanophotocatalyst for degradation of persistent pharmaceutical compounds such as naproxen, carbamazepine and theophylline in water treatment effluents. According to their results, higher temperature and higher pH favors the photodegradation of theophylline in presence of TiO_2 nanobelts and ultraviolet light. They also observed that after 90 min of reaction, more than 95 % of three compounds were degraded (Liang et al. 2013). Shirazi et al. used the TiO_2 nanoparticles with the average size of 21 nm to degrade carbamazepine from water in the presence of ultraviolet light. They achieved 85 % degradation after 36 min for carbamazepine in distilled water, but they observed that the removal efficiency declined to 30 % when the source of water was changed to groundwater. They attributed this reduction to the presence of divalent ions, such as SO_4^{2-} and CO_3^{2-} since these ions may adsorb onto the surface of the TiO_2 and prevent the generation of superoxide anion $O_2^{\bullet-}$ and hydroxyl radical $OH^{\bullet}$ (Shirazi et al. 2013). In Table 4.3, the reaction constants and water matrices in different degradation systems, which follow the pseudo-first order reaction, are listed. According to this table, the value of K largely influences the economy of the systems. For example, when K is higher than 0.1 min^{-1}, more than 95 % of the compound can be degraded within 30 min whereas for K less than 0.01 min^{-1}, only 16 % of the contaminant can be degraded within the same time. Therefore, developing systems with higher K value can decrease the capital and operational costs to a remarkable extent.

Table 4.3 Chemical transformation systems which follow a Pseudo-first-order kinetic model. The highest rate constant was reported for degradation of norfluoxetine by TiO_2 nanobelts and the lowest one was for polychlorinated biphenyls by zero-valent iron nanoparticles

Nanomaterials (conc. g/L)	Emerging contaminants	K_1	Water matrices	References
TiO_2 (4 g/L)	Alachlor	0.0017–0.0152	Distilled	Mahmoodi and Arami (2010)
	Fenitrothion	0.0015–0.0230		
TiO_2 nanowire membranes (1.25 g/L)	Trimethoprim	0.0269	Milli Q	Hu et al. (2011)
	Norfluoxetine	0.1239		
	Atorvastatin	0.0688		
TiO_2 nanobelts (0.2 g/L)	Naproxen	0.0616	Milli Q	Liang et al. (2013)
	Carbamazepine	0.0291		
	Theophylline	0.0912		
TiO_2 nanoparticles (0.02 g/L)	Carbamazepine	0.017	Groundwater	Shirazi et al. (2013)
		0.050	Distilled	
FeFNS-doped TiO_2 (0.03–0.3 g/L)	Diazinon	0.0162	Deionized	Hossaini et al. (2014)
Nitrogen and fluorine codoped TiO_2 (5 g/L)	Caffeine	0.0146	Milli Q	Barndõk et al. (2013)
	Carbamazepine	0.0125		
	Atrazine	0.0109		
Nano-magnetite (Fe_3O_4) (1–1.8 g/L)	Carbamazepine	0.00303	Distilled	Sun et al. (2013)
	Ibuprofen	0.00201		
Nanoscale zero valent iron (10 g/L)	Polychlorinated biphenyls	0.00183	Deionized	Chen et al. (2014)
Pd-Fe nanoparticles (10 g/L)	Polychlorinated biphenyls	0.002	Deionized	Chen et al. (2014)
Nanoscale iron particles (10 g/L)	Perchlorate	0.0253	Deionized	Cao et al. (2005)
Au-Pd-TiO_2 nanotube film (n.d.)	Malathion	0.0158	Twice-distilled	Yu et al. (2010)

The Pseudo-first-order equation can be expressed as:

$$Ln(C_t / C_0) = -k_1 t$$

Where: C_0 and C_t (mol/L) are concentrations of contaminant at different time, t (min) and k_1 (1/min) is reaction constant

4.1.3 Doped TiO_2

In order to increase the performance of TiO_2 nanophotocatalyst, researchers investigated the effect of doping TiO_2 with other elements such as iron, carbon and nitrogen. For example, Wang et al. synthesized anatase TiO_2 nanoparticles doped with iron and carbon (Fe/C-TiO_2) to degrade bisphenol A and clofibric acid in a photocatalytic process. They observed that Fe and C had synergistic effects on improving photocatalytic activities of Fe/C-TiO_2 as compared to C-TiO_2, Fe-TiO_2 and TiO_2 nanoparticles under simulated solar light and visible light irradiation. According to their results, no bisphenol A or clofibric acid could be detected after 4 h of irradiation with visible light by Fe/C TiO_2, and 61 % and 71 % of the total organic carbon were mineralized, respectively (Wang et al. 2011). Hossaini et al. doped TiO_2 with a mixture of iron and non-metal elements i.e. N, S and F for use in light emitting diodes-activated photocatalysis process for degradation of diazinon pesticide. Their analysis showed that the nanophotocatalyst comprised of mesoporous nanocrystals with the average size of 6.7 nm. They observed that the new nanophotocatalyst can improve the degradation of diazinon by 52.3 % compared to plain TiO_2 at neutral pH. Also, they reported that diazinon degradation increased from 44.8 to 96.3 % when the concentration of nanophotocatalyst increased from 25 to 300 % at a reaction time of 100 min (Hossaini et al. 2014).

Pelaez et al. used nonionic fluorosurfactant as pore template material to dope TiO_2 nanoparticles with nitrogen and fluorine. The new material employed contained mesoporous structure with pore size of 2–10 nm in photocatalytic process under visible light with λ higher than 420 nm for destruction of microcystin. They achieved the highest degradation rate of 70 % after 2 h at pH 3, and the electrostatic interactions between compound and the TiO_2 nanoparticles with nitrogen and fluorine nanosystem favored photocatalytic degradation. They concluded that co-doping TiO_2 with nitrogen and fluorine increased photocatalytic activity compared to TiO_2 nanoparticles with only fluorine or nitrogen doping (less than 20 % degradation) (Pelaez et al. 2009). In a similar study, Barndok et al. synthesized a nanosystem of TiO_2 nanoparticles (50 nm) doped with nitrogen and fluorine to remove atrazine, carbamazepine, and caffeine from water through a photocatalytic process using solar light. They performed their tests in synthetic water and also in an effluent from a hybrid biological concentrator reactor. The results showed that after 2 h of reaction, about 70, 75, and 80 % removal in synthetic water and about 50, 70, and 70 % removal in the biological concentrator reactor effluent was obtained for atrazine, carbamazepine, and caffeine (Barndõk et al. 2013). The presence of various complex ions, such as sulfate and chloride compete with target compounds in the photocatalytic process and therefore the efficiency of such system under real conditions is less than the one obtained under controlled conditions in laboratory.

TiO_2 nanoparticles are also studied for their adsorption capacity for contaminants. For example, Hristovski et al. studied the capabilities of aggregated TiO_2 nanoparticles for adsorption of arsenate from four different water matrices in a packed bed column. In their batch tests, TiO_2 nanoparticles achieved 98 % removal rate in all water matrices which is remarkable (Hristovski et al. 2007). In another study, Hristovski et al. transformed TiO_2 into bundle-like titanate nanofibers of rectangular in shape with ~4 um long and 30–100 nm thick in order to increase the adsorption capacity for arsenate. However, their experiment showed that commercial TiO_2 had 40 times more capacity in comparison to synthesized nanofibers and therefore they were less suitable for arsenate removal though they have unique surface chemistry and porosity (Hristovski et al. 2008a). In Tables 4.4 and 4.5, a summary of nanostructured adsorbent with their related parameters are listed. In Freundlich model, there is no maximum adsorption capacity because adsorbates can form multilayers around adsorbent. But in Langmuir and Polanyi-Manes models, there are maximum values for adsorption or sorption. Many of the proposed nano-

Table 4.4 Physical adsorption systems which follow Freundlich isotherm model. In Freunlich model. if $n<1$, then adsorption is a chemical process and if $n>1$, then adsorption is a physical process (Desta 2013). Therefore all of the processes in this table are physical except carbon nanotubes

Nanomaterials	Emerging contaminants	K_F[a]	1/n	Water matrices	References
TiO_2, Fe_2O_3, ZrO_2 and NiO nanopowders	Arsenic	1.37–12.09	0.21–0.52	10 mM $NaHCO_3$ nanopure water[b]	Hristovski et al. (2007)
Titanate nanofibers	Arsenic	5–26	0.51–0.66	10 mM $NaHCO_3$ buffered nanopure water	Hristovski et al. (2008a)
Nanostructured iron hydroxide	Perchlorate	2.5–34.7	<0.6	Distilled	Hristovski et al. (2008b)
	Arsenate				
Nanofiltration	Atrazine	0.04–11.58	0.5633–1.1196	Groundwater	Tepus et al. (2009)
	Deethylatrazin	0.05–0.75	0.5825–0.8387		
Carbon nanotubes	2-naphthol	0.128–0.222	1.1988–1.5193	Milli-Q	Xu et al. (2015)
Graphene oxide	Aniline	5.2–14.4	0.526–0.7519	Distilled	Yan et al. (2015)
	Nitrobenzene	6.8–11.1	0.4386–0.4673		
	Chlorobenzene	0.78–1.80	0.7407–0.8130		
Magnetic graphene nanoplatelets	Arsenic	4.32	0.3584	Deionized	Zhu et al. (2012)

[a] The freundlich isotherm model can be expressed as:

$$Q_e = K_F C_e^{1/n}$$

Where: C_e (mg/L) and Q_e (mg/g) are the equilibrium concentration of adsorbate in liquid and solid phase, n and K_F $(mg/g)(L/mg)^{1/n}$ are the adsorption equilibrium constant

[b] Conductivity <1μS cm^{-1}

Table 4.5 Physical adsorption systems which followed Langmuir or Polanyi-Manes isotherm models. The maximum adsorption capacity was reported for Triclosan on single-walled carbon nanotubes and the lowest one was reported for Trichlorophenol on magnetic nanoparticle

Nanomaterials	Emerging contaminants	Adsorption model	Maximum adsorption capacity	K_L or log K	Water matrices	References
Magnetic nanoparticles	2,4,6-Trichlorophenol	Langmuir	75.49	n.d.	n.d.	Pan et al. (2011)
MWCNT	Polychlorinated biphenyls	Langmuir	235–261	n.d.	Milli-Q	Shao et al. (2010)
SWCNT	Ibuprofen	Polanyi-Manes	231.5	5.61	Milli-Q	Cho et al. (2011)
	Triclosan		558.2	6.52		
MWCNT	Ibuprofen	Polanyi-Manes	81.6	4.43	Milli-Q	Cho et al. (2011)
	Triclosan		434.7	6.08		
O-MWCNT	Ibuprofen	Polanyi-Manes	19.4	3.89	Milli-Q	Cho et al. (2011)
	Triclosan		105.4	5.53		

The Langmuir isotherm model can be expressed as: $Q_e = (K_L Q_m C_e) / (1 + K_L C_e)$

Where: Q_m is the maximum adsorption capacity of the sorbent (mg/g), and K_L is the affinity constant

The Polanyi-Manes model (PMM) equation can be expressed as: $Q_e = Q_p^0 \exp(a(RT\,Ln(S_w / C_e)))^b$

Where: $Q_p{}^0$ is maximum sorption capacity (mg/g). a and b are model constants, R is the universal gas constant (8.314×10^{-3} kJ/mol/K), T is absolute temperature (K), and Sw is the solubility of the adsorbate in water at 20 °C

MWCNT Multiwalled carbon nanotubes, *SWCNT* Single-walled carbon nanotubes, *O-MWCNT* oxidized multiwalled carbon nanotubes

structured materials showed superior performance compared to their conventional counterparts. However the high cost of nanomaterials production and their limited life cycles are important challenges for their scale-up.

4.1.4 Magnetic Nanoparticles

Magnetic nanoparticles consist of magnetic elements, such as iron, cobalt and nickel in their chemical structure. Since these nanomaterials combine high surface area with magnetic properties, they can be easily isolated from solution by applying a magnetic field. Because of these interesting properties, magnetic nanoparticles have been the focus of much research in recent years for their potential use in catalysis and adsorption. For example, Shen et al. synthesized magnetic Fe_3O_4-C18 composite nanoparticles with the size of 5–10 nm for using in the clean-up and enrichment procedures of measuring organophosphorous pesticides by gas chromatography technique. According to their results, the composite nanoparticles have comparable recovery of 80–93 % to conventional C18 materials that is 82–94 % recovery while clean-up and enrichment procedures are faster and easier. They also observed that

Fe_3O_4-C18 composite nanoparticles is recyclable up to ten times with negligible loss of properties (Shen et al. 2007). In a similar study, Moliner-Martinez et al. incorporated Fe_3O_4 magnetic nanoparticles in a silica matrix for extraction and preconcentration of pharmaceutical compounds, such as aspirin, acetaminophen, diclofenac and ibuprofen from water without need of clean-up process. The recovery of this nanostructured sorbent was reported to be in the range of 80–110 % with relative standard deviation less than 12 %. Under the optimum conditions, the new sorbent material demonstrated suitable reusability during 20 uses with no loss in efficiency (Martínez et al. 2011).

Zhu et al. developed graphene with strong magnetic properties composites by decorating nanoplatelets with core-shell Fe-Fe_2O_3 nanoparticles. The new nanomaterial was used for removal of arsenate from water. They observed that at optimum pH (~7), the maximum adsorption capacity is around 11.34 mg/g that is much higher than other magnetic nanoparticles i.e. 1 mg/g (Zhu et al. 2012). Ghosh et al. studied the adsorption naproxen, carbamazepine and bisphenol A from aqueous solutions onto Fe_3O_4 nanoparticles that were coated with thiodiglycolic acid. They also grafted 6-deoxy-6-ethylenediamino-β-cyclodextrin onto the magnetic nanoparticles to compare the adsorption capacities. According to their results, the adsorption capacities of thiodiglycolic acid-coated nanoparticles with and without 6-deoxy-6-ethylenediamino-β-cyclodextrin graft were in the range of 0.24–0.38 mg/g and 0.90–1.30 mg/g. They suggested that Fe_3O_4 nanoparticles serve as magnetic separators and 6-deoxy-6-ethylenediamino-β-cyclodextrin provides the capability to adsorb pollutants through inclusive host-guest interactions (Ghosh et al. 2013).

Beside adsorption, magnetic Fe and Fe_3O_4 nanoparticles can act as catalyst in the degradation of emerging contaminants. Sun et al. used magnetic Fe_3O_4 nanoparticles with the average size of 30 nm for degradation of the carbamazepine and ibuprofen in aqueous suspensions. They concluded that at neutral pH, hydroxyl radical (•OH) produced form the decomposition of H_2O_2 on the Fe_3O_4 nanoparticle surface plays the major role in the degradation of carbamazepine and ibuprofen. They also observed that the degradation of carbamazepine and ibuprofen fitted with pseudo-first-order kinetics model with the rate constants (k) of 0.182 and 0.121 h^{-1}, respectively. In addition, the presence of montmorillonite can reduce the rate constant for carbamazepine due to adsorption at neutral pH, while it has no effect on ibuprofen due to electrostatic repulsion (Sun et al. 2013). In another investigation carried out by Cao et al. Iron nanoparticles showed capability to reduce perchlorate ($ClO^{-}{}_4$) to chloride. Under same conditions, they reported no reduction using microscale iron powder. They observed that by increasing temperature from 25 to 75 °C, the rate constant will increase from 0.013 to 1.52 (mg perchlorate/(g nanoparticles × h)) (Cao et al. 2005). Unfortunately, higher activation energy of perchlorate-iron reaction i.e. 79.02 ± 7.75 kJ/mol is not favorable for large scale applications.

Palladium is known for its catalytic properties towards conversion of harmful gases in automobile exhaust to less harmful compounds. Also, nickel is widely used as a catalyst in organic chemistry for hydrogenation. Therefore, the idea of using these two metals in combination with iron nanoparticles for degradation of contaminants has led to interesting results. Chen et al synthesized iron/palladium (Fe/Pd) bimetallic nanoparticles to catalyze the degradation of 2, 2′, 4, 4′, 5, 5′-hexachlorobiphenyl in deionized water. According to their results, the degradation efficiency for bimetallic nanoparticles and iron nanoparticles were 93.8 % and 74.9 % after 20 h of reaction. Later, they applied the results to the two soil samples collected from an electrical waste recycling area that was contaminated with polychlorinated biphenyls. They observed 53.4–81.5 % removal efficiency of polychlorinated biphenyls from soil by Pd/Fe nanoparticles that was higher than 48.3–64.6 % removal efficiency reported for iron nanoparticles (Chen et al. 2014).

In a similar study, Lien et al. produced iron nanoparticles in the size range of 1–100 nm for catalytic transformation of chlorinated methanes e.g. CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl. They also deposited palladium at the loading of 0.05–1 % Pd by weight on the surface of iron and compared the capabilities of these two nanoparticles and also commercial iron particles with the average size of 10 µm in reaction with chlorinated methane. They observed that after 1 h of reacting 0.1 mM of CCl_4 or $CHCl_3$, there was no detectable reactant in the case of palladized iron nanoparticles. In these reactions, methane and CH_2Cl_2 were the major end products at the yields of 52 % and 23 %, respectively. However, iron nanoparticles and commercial iron particles exhibited much slower reactions of chlorinated methanes. The kinetic analyses revealed that the surface area-normalized rate coefficients (k_{SA}) for palladized iron nanoparticles was two orders of magnitude greater than those for iron nanoparticles and commercial iron particles (Lien and Zhang 1999). In another attempt, Vijayakumar et al. synthesized iron-nickel (Fe-Ni) nanoparticles in the size range of 36–41 nm and immobilized them on to a polysulphone support to use as a catalyst for the reduction of dichloroethane ($C_2H_4Cl_2$) and trichloroethylene (C_2HCl_3). They observed 90 % removal after a 36 h reaction with the initial concentration of 26.81 and 682.81 ppb for $C_2H_4Cl_2$ and trichloroethylene C_2HCl_3 respectively. According to their study, in alkaline pH, Fe–Ni nanoparticles lose their catalytic properties and cannot get involved in the hydrodechlorination of target compounds (Vijayakumar et al. 2012). Shirazi et al. used iron nanoparticles in the size range of 8–18 nm for degradation of carbamazepine in water in the presence of H_2O_2. They obtained 78.5 % total organic carbon removal after only 5 min in the presence of 10 ppm iron nanoparticles and 25 ppm H_2O_2. In contrast to their result for TiO_2/ultraviolet process, no difference in performance was observed when water source was changed from distilled water to groundwater (Shirazi et al. 2013).

4.1.5 Precious Metal Nanosystems

Gold (Au) and Silver (Ag) nanoparticles are widely used in different applications, such as sensors, catalysis, electronics and medicals. Removal of emerging contaminants from water sources is another application of precious metals that has attracted the attention of researchers (Jain et al. 2016; Dasgupta et al. 2016a, b). For example, Das et al. produced gold nanoparticles with 10 nm in diameter through biosynthesis and used them for adsorption of organophosphorous pesticide, such as malathion and parathion from aqueous solutions. They observed that synthesized nanoparticles could remove almost all of the tested pesticides after 30 min (Das et al. 2009). In another study, Suman et al. produced Ag nanoparticles and embedded them within the porous concrete pebble particles. They also synthesized nanocellulose by acid hydrolysis of cellulose and used these two nanoparticles for removal of microbes (*Escherichia coli*) from water. They used a column with two beds of nano embedded Ag nanoparticles and one bed of nanocellulose in between for continuous purification of water and observed 99 % decontamination of microbes at pH 6. According to their proposed mechanism, Ag nanoparticles kill microorganisms and prevent formation of biofilm and nanocellulose can adsorb dye and heavy metals and the column can be reused up to five cycles with no loss in performance (Suman et al. 2014).

Li et al. observed that the gold Au-coated TiO_2 nanotube arrays show recyclability as a substrate for surface-enhanced Raman spectroscopy. Interestingly, this new system can clean itself through photocatalytic degradation under ultraviolet light. However, recycling process is time consuming (30 min), and only highly trained staff can performed test with this new substrate (Li et al. 2010). Yu et al. developed a nanosystem by modification of TiO_2 nanotube film with Au and Pd (Au-Pd-TiO_2) to degrade malathion, which is an organophosphorus pesticide, through photocatalytic process in the presence of ultraviolet light. Their experiments showed that Au and Pd can increase the degradation rate by 172 % compared to naked TiO_2 nanotube film and attributed this behavior to effective separation of generated charge carriers and also the higher generation rate of H_2O_2 (Yu et al. 2010). Han et al. formed Ag nanoparticles with a diameter of 5.9 ± 1.2 nm on TiO_2 aggregates to use for the photocatalytic degradation of the antibiotic oxytetracycline under ultraviolet -visible light irradiation. They observed that by increasing the load of Ag, the absorption in the visible light region increased. However, under both ultraviolet -visible light and visible light illumination, the highest photocatalytic activity for the degradation of oxytetracycline was observed at 1.9 wt.% of Ag loading so that it took 2 h for ultraviolet -visible and 3 h for visible light to reach below the detection limit of gas chromatography analysis (Han et al. 2014).

4.1.6 Carbon Nanotubes

Carbon nanotubes are categorized into single-walled carbon nanotubes and multi-walled carbon nanotubes according to their atom layers in the walls of carbon nanotubes. The diameter of single-walled carbon nanotubes range from 0.3 to 3 nm, whereas the multi-walled carbon nanotubes have concentric arrangement of cylinders and their diameters can reach up to 100 nm (Balasubramanian and Burghard 2005). Carbon nanotubes have attracted attention of many researchers due to their outstanding structural, chemical and mechanical properties (Miyagawa et al. 2005; Popov 2004). Besides application in electronics, sensors, catalysis, and composite materials, carbon nanotubes showed a promising application as adsorbent material for different contamination due to their large surface area and also tubular structure (Balasubramanian and Burghard 2005; Polizu et al. 2006). However, there are different parameters including surface chemistry of carbon nanotubes, the chemical properties of contaminants, and the chemistry of aqueous solution including pH, ionic strength and presence of other compounds that can affect the adsorption of contaminants onto carbon nanotubes.

Zhou fabricated a column of multi-walled carbon nanotubes as a sorbent for atrazine and simazine in the pre-concentration process for measuring these compounds using HPLC in water samples. The recovery of two compounds were in the range of 82.6–103.7 % in spiked samples (Zhou et al. 2006). Shao et al. used multi-walled carbon nanotubes grafted with β-cyclodextrin to remove polychlorinated biphenyls from water under ambient conditions. In their experiments, multi-walled carbon nanotubes grafted with β-cyclodextrin showed higher adsorption capacity (95 % removal) compared to multi-walled carbon nanotubes (90 % removal) (Shao et al. 2010). In a similar study, Salipira et al. tried to adsorb *p*-nitrophenol from water using a copolymer of cyclodextrin cross linked by 5 % of functionalized carbon nanotubes. The new material could remove 99 % of model compounds from 10 ppm spiked samples, whereas granular activated carbon and native cyclodextrin could remove only 47 % and 58 %, respectively. The new nanomaterial could maintain its adsorption capacity after at least 18 cycles (Salipira et al. 2007). In another study, they used the new copolymer to adsorb trichloroethylene and achieved 98 % removal efficiency (Salipira et al. 2008).

Chen et al. combined TiO_2 nanoparticles with multi-walled carbon nanotubes to enhance the photocatalytic degradation of atrazine under microwave irradiation rather than ultraviolet light. According to their results, the new composite material showed 20–30 % higher efficiency compared to TiO_2 alone. They attributed this improvement to the strong capability of the new material to absorb microwaves (Chen et al. 2011). Cho et al. studied the adsorption of ibuprofen and triclosan by single-walled, multi-walled and oxidized multi-walled carbon nanotubes from water under conditions close to natural environment and water treatment systems. They concluded that for hydrophobic compounds, single-walled carbon nanotubes have higher adsorption capacity than multi-walled ones due to larger specific surface area, while oxidized multi-walled carbon nanotubes showed lower capacity compared to not oxidized ones due to higher surface oxygen. They also indicated that for pHs below pKa, adsorption capacity was higher due to lack of electrostatic repulsion (Cho et al. 2011).

Zhang et al. studied the sorption kinetics of tetrabromobisphenol A onto raw and functionalized multi-walled carbon nanotubes in aqueous solutions using a pseudo-second-order model, an intraparticle diffusion model and Boyd model. According to their results, both types of multi-walled carbon nanotubes showed rapid binding for tetrabromobisphenol A within 20 min and the kinetics could be described by the pseudo-second-order model. Also, the external diffusion (boundary layer diffusion) was considered as the rate-limiting step (Zhang et al. 2014).

Xu et al. developed a new adsorbent by self-assembling carbon nanotubes onto $CaCO_3$ micro-particles in shell-core structure and studied its capacity for removing

2-naphthol, naphthalene and 4-chlorophenol from aqueous solutions. They observed that with increasing carbon nanotubes loading, the adsorption coefficient (K_f) increased but the normalized adsorption coefficient (K_{fCNT}) decreased (Xu et al. 2015). Srivastava et al. fabricated carbon nanotube filter that consisted of hollow cylinders with radially aligned carbon nanotubes walls and used it for removal of bacterial pathogens (*Escherichia coli* and *Staphylococcus aureus*) and Poliovirus sabin 1 from water. This new filter was easily re-usable by ultrasonication or autoclaving (Srivastava et al. 2004).

4.1.7 Graphene Nanoplatelets

Graphene is a new member of the carbonaceous nanomaterials group that has a 2D (Fig. 4.3) honeycomb structure (sp^2-hybridization) with a thickness of one carbon atom. Graphene can be considered as a building block for other carbonaceous nanomaterials, such as fullerene and nanotubes. Due to large theoretical specific surface area and especially highly hydrophobic surface, graphene shows strong adsorption affinity to hydrophobic organic pollutants, such as polycyclic aromatic hydrocarbons, chlorobenzenes, antibiotics, pesticides and phenols (Liu et al. 2014; Wang et al. 2014). After increasing awareness about the potential threats of emerging contaminants, researchers considered graphene as a promising solution to address the problem of removing these contaminants at lower concentrations.

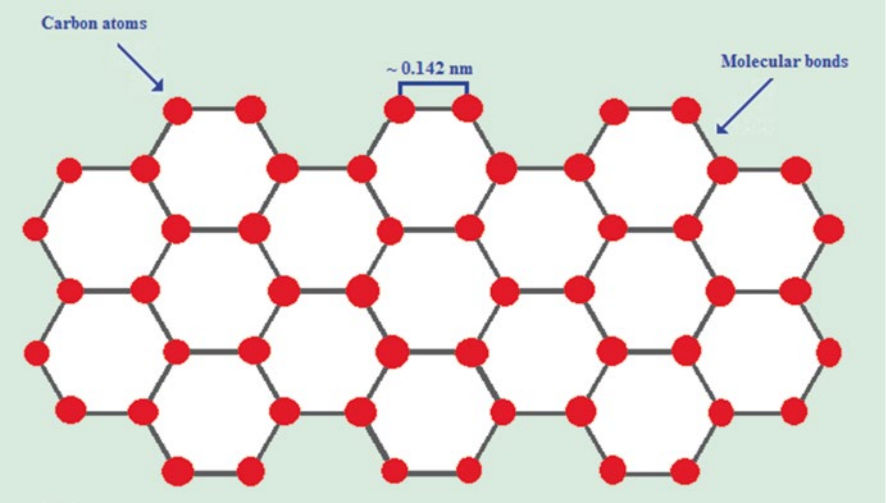

Fig. 4.3 Schematic of the structure of graphene nanoplatelets. The carbon-carbon bond length in graphene is around 0.142 nm and Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm. Owing to its two-dimensional structure, Graphene has a theoretical specific surface area of more than 2600 m^2/g which is much larger than that reported to date for carbon black or carbon nanotubes (Bonaccorso et al. 2015)

For example, Al-Khateeb et al. studied the removal of aspirin, acetaminophen, and caffeine from aqueous solution by graphene nanoplatelets. Their results showed that pH 8 is the optimum pH and more than 94 % of all compounds can be removed within 10 min at the graphene loading of 1 g/L. They also calculated the thermodynamic parameters (ΔG, ΔH and ΔS) of adsorption process and concluded that for the studied compounds, the process is spontaneous at all temperatures (Al-Khateeb et al. 2014).

Several researchers tried to compare the performance of graphene with other adsorbent materials, such as granular activated carbon, carbon nanotubes and also other graphene based nanomaterials. For example, Rizzo et al. coupled conventional sand filtration with graphene adsorption system to remove pharmaceutical compounds from municipal wastewater. Using this system, they achieved more than 95 % removal for caffeine, carbamazepine, ibuprofen and diclofenac while in same conditions, granular activated carbon showed only 63 % removal for mixture of pharmaceutical compounds. They also observed that graphene treatment can decrease toxicity towards *Daphnia magna* with 0–50 % immobilization (Rizzo et al. 2015). In a similar investigation, Zhu et al. compared graphene with granular activated carbon system for adsorption of ciprofloxacin and observed 77 % greater adsorption capacity for graphene (323 mg/g) compared to granular activated carbon (180 mg/g). According to the FTIR spectroscopy, they suggested that adsorption of ciprofloxacin on graphene primarily occurred through π-π interaction. Interestingly, they observed that ionic strength, presence of natural organic matter, and different water sources were less important for graphene than granular activated carbon (Zhu et al. 2015). In another study, Balamurugan and Subramanian compared the adsorption of the homologues series of chlorobenzenes with the molecular formula of $C_6H_mCl_n$ where m and n = 0–6, and m + n = 6 onto graphene sheet and single-walled carbon nanotube. They found that graphene has higher adsorption capacity for chlorobenzenes compared to single-walled carbon nanotube that is due to planar geometry of graphene that facilitates the surface adsorption of compounds (Balamurugan and Subramanian 2013). Also, Liu et al. compared three different graphene with single-walled carbon nanotube to remove ketoprofen, carbamazepine, and bisphenol A from water under different solution conditions. They observed that the adsorption isotherms were consistent with the orders of the surface areas and micropore volumes of adsorbents and therefore in all cases, single-walled carbon nanotube showed the best performance. Their results also suggested incomplete occupation onto adsorption sites of graphene as a result of the aggregation of sheets and the presence of remaining oxygen-containing functionalities (Liu et al. 2014).

Some researchers attached oxygen containing groups to graphene using strong oxidizers to enhance the functionality of graphene as adsorbent. These new nanomaterials are called “graphene oxide”, however in several cases; they are reported to have lower adsorption capacity compared to pristine graphene. For example, Wang et al. synthesized graphene and graphene oxide nanosheets and compared their performance for adsorption of naphthalene from water. They observed that attaching oxygen-containing groups to graphene can severely decrease the affinity of polycyclic aromatic hydrocarbons to graphene which is dominated by π-π interactions and the sieving effect formed by wrinkles on graphene surfaces. In fact, by attaching the new groups, the grooves on the graphene surface disappeared and π-π interactions will be restricted (Wang et al. 2014). Also, Yan et al. synthesized graphene oxide for the removal of aniline, nitrobenzene, and chlorobenzene, from water. They concluded that hydrophobic interactions (π-π stacking and hydrophobic effects) between graphene oxide and adsorbates played major role in the whole adsorption process. Also, they studied the effect of oxidizing extent of graphene on adsorption capacity and observed that moderately oxidized graphene with around 50 % graphitic zone had the best adsorption performance due to good dispersibility and enough activated adsorption sites (Yan et al. 2015). Kyzas et al. synthesized a nanocomposite from graphite oxide, which is the precursor of graphene, and modified chitosan for the removal of dorzolamide, that is a pharmaceutical compound, from biomedical synthetic wastewaters. They suggested that the reactive groups of graphite oxide and chitosan have interaction with the amino groups in dorzolamide molecule which enhanced adsorption capacity. The maximum adsorption at optimum pH (~3) was 334 mg/g which was superior compared to graphite oxide (175 mg/g) and chitosan (229 mg/g) (Kyzas et al. 2014).

4.1.8 Polymeric Nanosponge

Mhlanga et al. produced cyclodextrin polymer with nanosponge structure using bifunctional isocyanate linkers to remove a series of chlorinated disinfection byproducts and an odor-causing compound, in water 2-methylisoborneol. The as-synthesized polymer could adsorb the pollutants with more than 99 % efficiency at ng/l level which was superior to granular activated carbon (Mhlanga et al. 2007). Later, they reported the removal of n-nitrosodimethylamine from drinking water, using this nanosponge polymer with 80 % efficiency (Mhlongo et al. 2009). The high efficiency of this polymer was due to the inclusive host-guest interactions between polymer and contaminants which is shown in Fig. 4.4. However, nanosponge structures will be saturated after sometime and researchers should also investigate their recyclability.

Arkas et al. impregnated TiO_2 porous ceramic filter with nanosponge made from functionalized poly (propylene imine) dendrimer, poly (ethylene imine) hyperbranched polymer, and β-cyclodextrin derivatives to remove contaminants from water at ppb level. Their results showed that by using this new class of filter system, polycyclic aromatic hydrocarbons can be removed efficiently (higher than 95 %) and other contaminants, such as trihalogen methanes, monoaromatic hydrocarbons, and pesticides were also removed efficiently (higher than 80 %) (Arkas et al. 2005, 2006).

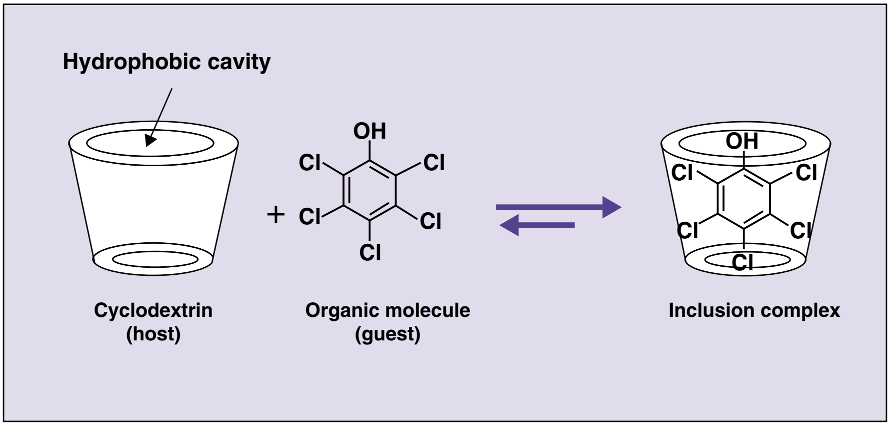

Fig. 4.4 A schematic for host-guest interaction. In this mechanism, the host material has free spaces in its structure which is perfect for retaining the guest molecules through non-covalent forces including hydrogen bonds, ionic bonds, van der Waals forces, and hydrophobic interactions

4.1.9 Nanofiltration Membranes

Separation processes through nanofiltration membranes have been increasingly considered as an affordable and reliable technology for the purification of water from unconventional sources, such as contaminated surface water, brackish water, and secondary effluent of wastewater treatment plants where micropollutants should be removed according to regulations. Nanofiltration membrane has pore size of less than 2 nm or molecular weight cut-off in the range of 200–500 Da. Therefore, nanofiltration membranes are capable of removing pollutants having molecular weights larger than molecular weight cut-off of membrane. In Fig. 4.5, the performance of different filtration technologies is illustrated. According to this figure, reverse osmosis membrane retained all the solutes, even monovalent ions, which was not necessary and their operational costs are also high. On the other hand, ultrafiltration membranes can only retain microorganisms and proteins and they are not capable of filtering molecules with MW of less than 2000. Therefore, nanofiltration membranes could fill this gap with reasonable cost and reliable performance. At the present time, nanofiltration membrane modules are working in some water treatment plants in the world for removing or reducing contaminants. For example, in Cooper city, Florida, a drinking water treatment plant was upgraded in 1998 with nanofiltration membrane module with the capacity of 11,000 m^3/day and is capable of producing high quality drinking water.

In some cases, the removal efficiency for certain compounds with nanofiltration membranes is more than 98 %. However, besides size exclusion, there are several parameters, such as electrostatic charge repulsion, hydrophobic interaction and membrane fouling that can increase or decrease the rejection of contaminants. In

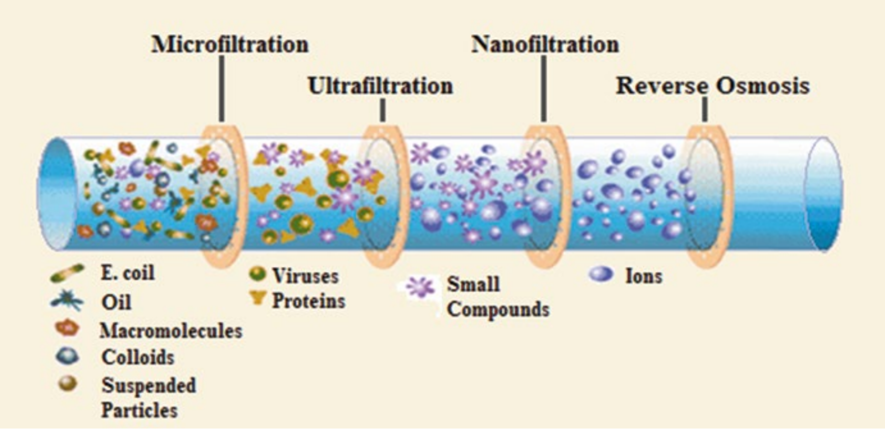

Fig. 4.5 Performance of nanofiltration membrane compared to other filtration technology. Nanofiltration can retain up to 98 % of the organic contaminants but let the ions pass through the membrane. Therefore it can be implemented for drinking water decontamination

recent years, many researchers tried to understand the mechanisms of solute transport in nanofiltration membranes so that they could select the best option for remediation of specific water source (Nghiem et al. 2005, 2010; Simon et al. 2012; Verliefde et al. 2007a; Yüksel et al. 2013; Zhang et al. 2006). For example, Verliefde et al. studied the removal of different emerging contaminants using a nanofiltration system with negatively charged surface. They concluded that the size exclusion is the dominants mechanism for rejection of neutral compound such as carbamazepine, but for negatively and positively charged compounds such as ibuprofen and atenolol, electrostatic repulsions and attractions can affect the rejection (Chellam and Taylor 2001; Verliefde et al. 2007b). Interestingly, Nghiem et al. observed by increasing the pH to above the pKa of the compounds, they transform from neutral to negatively charged species and therefore the rejection of the compounds will be higher through nanofiltration membranes with negatively charged surface (Nghiem et al. 2005, 2006).

Zhang et al. used nanofiltration membrane to remove bisphenol A from drinking water and observed that at the beginning of filtration the rejection rate was more than 90 % but after several hours, due to the saturation of membrane, the rejection rate decreased to 50 % (Zhang et al. 2006). Tepus et al. studied the effect of pressure on rejection rate of atrazine through nanofiltration membrane and observed that by increasing the pressure from 2 to 12 bar, the rejection rate will decrease from 60 to 50 % (Tepus et al. 2009). Also Yuksel et al. used nanofiltration membrane for removal of bisphenol A from water and achieved 80 % removal during 4 h of filtration (Yuksel et al. 2013). In another study, Ahmad et al. investigated the performance of four different nanofiltration membranes for removal of atrazine and observed that the rejection rate was in the range of 60–95 % for different membranes. They also observed that increasing the transmembrane pressure can lead to enhanced solute rejection and permeate flux (Ahmad et al. 2008). Therefore, the characteristics of membranes including material, molecular weight cut-off and surface charge are very important in determining the rejection rate of membrane for each compound.

To sum up, nanofiltration membranes can show high rejection efficiency for a wide range of emerging contaminants, although their performances are impacted by different parameters. But as a rule of thumb, bigger molecules with negative charge and higher hydrophilicity are rejected more efficiently.

4.2 Conclusion

Emerging contaminants are going to become a big challenge to the environment and human health in the near future and therefore, to prevent from their adverse effects, having efficient methods for their removal from different media, especially water and wastewater is of higher importance. Conventional wastewater treatment plants are not able to remove these contaminants from wastewater or they only shift them to soil through biosolids. Hence, novel methods are necessary to remove them at maximum level. Meanwhile, nanotechnology is the most likely tool to develop the solutions for contaminated media and there are numerous research works in this field. Generally there are physical methods, such as adsorption systems and chemical methods, such as photocatalytic degradation which enhance their performance through nanostructured materials. For example, carbon nanotubes with their large specific surface areas showed a promising performance in adsorbing contaminants even at low concentrations and TiO_2 nanophotocatalyst proved to be capable of near complete mineralization of contaminants. Also, nanofiltration membranes showed the ability to filter some emerging contaminants with more than 95 % efficiency. However, there are several drawbacks including the high cost of nanomaterials production, limited recyclability, sensitivity to interferences and toxicity of by-products that should be addressed before commercialization. Therefore, further research may result in better understanding of the mechanisms controlling emerging contaminants removal in different processes and finding solutions for current issues. Also, developing combinational systems which integrate physical separation and chemical transformation into one solution may attract the attention of researchers in future due to their potential to overcome the drawbacks of single process methods.

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Chapter 5
Nanosensors for the Detection of Pathogenic Bacteria

Anurag Jyoti, Rajesh Singh Tomar and Rishi Shanker

Abstract The consumption of microbiologically unsafe water poses major health threats and leads to several diseases like diarrhea, typhoid and cholera. Hence, the management of water quality is a growing need for public health and environment in the developing world. Existing methods for pathogen detection face challenges of inadequate monitoring in terms of specificity, rapidity and simplicity. Molecular methods including polymerase chain reaction (PCR) and its advanced version real-time PCR can detect pathogens at low levels. However, the requirement of sophisticated instrumentation and trained personnel makes these methods less applicable to field situations. The detection of target pathogens needs improvements to overcome existing drawbacks and should be based on simple, rapid, sensitive and specific methodologies.

Here, nanotechnology provides solutions such as biodiagnostics, where nanoparticle-based assays allow to specifically detect bioanalytes of clinical interest. Gold nanoparticles are promising materials because they have unique optical properties and high surface areas. Nanobiosensors are specific molecular-recognition probes that target an analyte, then convert that recognition into a measurable signal. Aptamers are single-stranded oligonucleotides that can fold into three-dimensional conformations. Aptamers have the unique property of binding specifically to a target molecule. As molecular recognition probes, aptamers in conjugation with gold nanoparticles have binding affinities and specificities that are can be explored to capture and identify specific pathogens. This chapter reviews practical applications of aptamer-conjugated nanoparticles for the detection of pathogenic bacteria.

Keywords Aptamers • Detection of pathogenic bacteria • Nanosensor • Gold nanoparticle • *Salmonella* • *Escherichia coli* • Immunoassay • Real-time PCR

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5.1 Introduction

The degradation in the microbiological quality of water and food adversely affects human health worldwide. Rapid population growth has placed new challenges on management of the frequency of food and water-borne disease outbreaks. The majority of water and food borne infectious diseases occur include diarrhea, typhoid, and cholera among others (Tomar and Jyoti 2015). An estimated 94 % of the diarrheal burden of disease is attributable to the environment, and associated with risk factors such as unsafe drinking water, lack of sanitation and hygiene (Prüss-Üstün and Corvalán 2006). Diarrhea is among the three most common causative agents of death in children under-5. It is responsible for almost 13 % deaths in this age-group, killing approximately 300,000 children in India each year (Lakshminarayanan and Jayalakshmy 2015). Approximately, 20 million episodes of travelers' diarrhea occur annually and out of which 80 % of cases are due to bacterial agents. Diarrheagenic *Escherichia coli*, including enterotoxigenic *E. coli* and enteroaggregative *E. coli*, are responsible for approximately 50 % of cases. Globally, the three regions can be alienated depending upon the risk of acquiring travelers' diarrhea for visitors. India is categorized under the high risk area, having 30–50 % chances of acquiring diarrhea (DuPont 2005). Enterotoxigenic *E. coli* is among the most common *E. coli* diarrheal pathotypes. In the developing countries about 0.7 million childhood deaths due to ETEC diarrhoea are reported every year (Pavankumar and Sankaran 2008). Enterohemorrhagic *E. coli*, a potential pathovar of *E. coli,* causes bloody diarrhea and hemorrhagic colitis. They can cause hemolytic uremic syndrome, an important cause of childhood acute renal failure (Tarr et al. 2005).

It has been documented that countries in south Asia, particularly south-east Asia, exhibit high burden of typhoid fever. India and neighboring countries have been identified as high risk sites for infections caused by *Salmonella* spp. Ochiai et al. (2008).

Despite ongoing efforts, the 2002 Millennium Development Goal of halving the population without clean water or sanitation by 2015 is unlikely to be achieved. Therefore, infectious waterborne diseases acquired through these uses are of supreme importance. Recent reports indicate that waterborne diseases of fecal-oral origin (mostly acute gastroenteritis) are the most common based on the number of people affected (WHO 2008; Stevens et al. 2009). The outbreaks have an enormous impact on the burden of diseases and sustainable development in developing countries. In contrast, the populations of developed countries are generally protected by legislation and regulations regarding water quality usage.

Globally, the source of almost the two third of the drinking water consumption is surface water, which may easily be contaminated by sewage discharges, animals defecation, faulty infected channels, municipal wastes and industrial effluents (Ahmed et al. 2005; Hamelin et al. 2006; Orsi et al. 2007). These surface waters harbor a variety of pathogens such as Shiga Toxin producing *Escherichia coli*, Enterotoxigenic *Escherichia coli* and *Salmonella* (Belanger et al. 2002; Shelton et al. 2006; Lothigius et al. 2010; Sur et al. 2007; Fong et al. 2007; Jyoti et al. 2010). Diseases caused by food-borne microbial hazards constitute a world-wide public health concern, despite the enormous volume of food produced and consumed safely throughout the world on a daily basis. During the past decades, the incidence of certain food-borne diseases has increased in many parts of the world despite the many improvements made to public health and food safety systems. Statistics indicate that even in industrialized countries one out of every three people has a food-borne microbial illness event every year (WHO 2003). It is recognized that food safety is not an absolute but rather a continuum of more or less safety and also that food-borne microbial hazards are likely to remain or (re-)emerge over time for a number of reasons. These include microbial adaptation, changes in the food production systems, changes in human demographics and behaviour, international travel and trade.

Global data indicate that the epidemiology of food-borne diseases is changing and that an increased range of microorganisms and foods are the leading cause of food-borne illness. A better understanding of the distribution, epidemiology and threat posed by emerging and uncharacterized pathogens is needed due to rapid, poorly controlled global spread through the food chain and ultimately and communities. The detection, reporting and characterization of food- and water-borne illnesses play an important role in identifying the origins and incidence of disease when links can be made to the causative agents and the foods involved.

Prevalence of pathogenic bacteria is well documented in drinking water. A better understanding of monitoring and detection system can lead to the minimization of risks imposed by the consumption of drinking water. Recently more emphasis has been given on the detection of pathogens in water. A number of methods exist for the detection of pathogenic bacteria in water having their own pros and cons (Fig. 5.1).

These include culture based and biochemical methods. These methods are labour intensive and time taking. Often these are qualitative which limit their applicability in recommendations in therapeutics (Li and Gu 2011). Polymerase Chain Reaction (Navas et al. 2006) and immunological techniques like Enzyme Linked Immunosorbent Assay are restricted to the laboratory set up (Crowther 1995).

Quantitative real time Polymerase Chain Reaction assays have proved to be sensitive and specific for the detection of *E. coli* and Salmonella serovars (Ram et al. 2008a; Jyoti et al. 2010). Due to the requirements of specialized instrumentation and trained personnels this technique has been limited to lab conditions only.

Nanomaterials mediated DNA detection are attractive alternative to the existing methods. Replacing fluorescently labeled DNA probes with metallic nanoparticles conjugated DNA probes are promising because they minimize the necessity of using expensive and complex instrumentation. Nanomaterials are attractive probe candidates because of their contrasting physical and chemical features. Their small size leads to unique large surface-to-volume ratio, often make them feasible to attach with nucleic acids. Gold nanoparticles, in particular, have surface plasmon resonance related optical absorption at around 525 nm and possess a red colour in an aqueous suspension. The gold nanoparticles are attached with the single stranded DNA (complementary to target DNA) to generate probe. Synthesised gold nanoparticle probes are allowed to hybridise with target DNA. As a result of

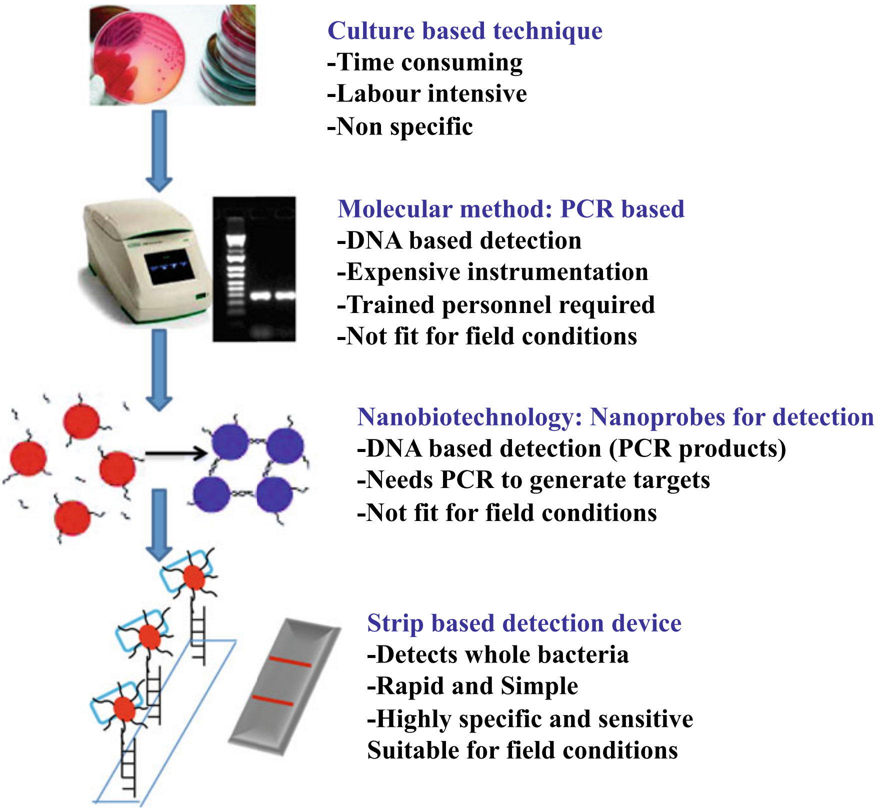

Fig. 5.1 Schematic representation of the development of pathogen detection systems

hybridization, a polymer network is formed. This condensed network brought the conjugated gold nanoparticles self assemblies into aggregates leading to change in colour from red to purple (Jyoti et al. 2011). The aforesaid reports track only the short synthetic oligonucleotides (up to 20–30 bp) targets, which again do not represent the sequences of a pathogenic DNA or PCR product.

In order to enhance the target detection capabilities, a number of gold nanoparticle based lateral flow immunoassays have been reported for the detection of bacterial pathogens but most of these assays are not in actual use. Applications of aptamers have proven to be very useful in the detection system. Gold nanoparticles conjugated with aptamers have unique capability to detect whole of the target bacteria without isolating its DNA.

Therefore, this paper intends to review the existing methods for the detection of pathogenic bacteria. The review also focuses onto the applications of gold nanoparticle and aptamer for the development of diagnostic device useful in field conditions for point-of-care diagnostics. It discusses the challenges and opens the avenues for future research. Therefore, the recent focus is on the development of rapid detection techniques, which are user friendly, require less technical expertise and time efficient.

5.2 Prevalent Water and Food Borne Pathogenic Bacteria

Water and food-borne bacterial agents have been the most well investigated and monitored causes of intestinal infectious disease. In developed countries, the risk assessment is being regulated, but still the disease burden is substantial. For the past two decades, *Salmonella* spp. and *E. coli* are among the three most persistant food borne pathogens. The serotypes of both these pathogens are responsible for majority of burdens of food and water borne illnesses (Newell et al. 2010).

5.2.1 Salmonella

Salmonella spp. is one of the most prevalent food and water borne pathogens, which causes morbidity and mortality in rural and urban settings. The pathogen causes salmonellosis, leads to significant medical and economic losses throughout the world (Voetsch et al. 2004). The causative organism can pass through the food chain from primary production to ultimate consumers and causes gasteroenterititis.

Salmonellae are gram-negative, rod-shaped, non-spore forming, mainly motile enterobacteria. They are facultative anaerobes; belong to *Enterobacteriaceae* family having dimensions around 0.7–1.5 μm (diameters) and 2–5 μm (lengths) (Madigan et al. 2009). *Salmonellae* can grow at optimum temperature between 35 and 37 °C, but growth has also been observed at temperatures ranging from 5 to 47 °C. The optimum pH for growth is near 7.0, but growth may occur between pH 4.0 and pH 9.0 (Lanata 2003). *Salmonellae* produce hydrogen sulfide, decarboxylate lysine and ornithine, and do not hydrolyze urea. They are oxidase negative and catalase positive and can grow on citrate as the sole carbon source.

The Centre for Disease Control and Prevention has distinguished two *Salmonella* species (or subgenera): *S. enterica* and *S. bongori. S. enterica* is further divided into six subspecies, of which *S. enterica* subsp. *enterica* is the most clinically significant, causing 99 % of *Salmonella* infections (Brenner et al. 2000). WHO report confirms there are 2579 serovars of *Salmonella*, out of which approximately 59 % belong to *S. enterica* subsp. enterica (Grimont and Weill 2007).

The pathogenicity of *Salmonella* serotypes vary widely. Most *Salmonella* virulence factors are clustered on chromosome referred as *Salmonella* pathogenicity islands (Shea et al. 1996). So far five *Salmonella* pathogenicity islands have been identified which encode different secretion systems required by pathogenesis (Schmidt and Hensel 2004). Typhimurium, Enteritis, Newport, and Heidelberg were among the top four most commonly isolated serotypes from human infections. These are also the most frequently isolated serotypes from food samples (CDC 2003). The pathogenicity of *Salmonella* requires the expression of virulent genes. Serotypes, not possessing the *invABC* genes are unable to invade mammalian cells (Galan 1996). Virulent chromosomal genes such as *invA* sequences unique to this genus and has been proved to be a suitable Polymerase Chain Reaction target with potential diagnostic application (Malorny et al. 2003; Zahraei et al. 2007; Jamshidi et al. 2008). This gene is recognized as an international standard for detection of *Salmonella* genus (Malorny et al. 2003).

Infection of *Salmonella* in immune-compromised persons causes Salmonellosis. The symptoms including diarrhea, fever and abdominal cramps develop within 3 days after infection, the illness may last 4–7 days (FDA/CFSAN 2008). In severe cases, the *Salmonella* infection may become systemic and spread from intestines to other body sites through blood stream and can cause death. The type of *Salmonella* usually associated with infections in humans is non-typhoidal *Salmonella*. It is usually spread from sources such as: infected poultry, eggs, egg products, cattle, milk and contaminated fruits and vegetables. Another form of *Salmonella*, typhoidal *Salmonella* can lead to typhoid fever. It is carried only by humans and is usually spread through direct contact with the infected person and its fecal matter. The infectious dose of *Salmonella* varies and depends upon serovars, source of infection and host susceptibility. In general, the minimum infective dose of *Salmonella* is 10^6 and *S.* Typhimurium 10–100 cells (Lanata 2003).

Salmonella is constantly released into the environment from infected humans, farm animals, pets, and wildlife (Baudart et al. 2000). The organism is frequently isolated from surface and potable water which serve as bacterial reservoirs (Chao et al. 1987; Jyoti et al. 2010). *Salmonella* has the ability to grow and survive in harsh conditions too as it can survive for 10–15 days in a septic system (Parker and Mee 1982).

5.2.2 Diarrheagenic *Escherichia coli*

E. coli is gram-negative, facultative anaerobic and non-sporulating bacterium and is generally rod-shaped. *E. coli* generally grows at 37 °C but some strains can grow upto 49 °C (Fotadar et al. 2005). Diarrheagenic *E. coli* causes the diarrhea in infants, children and immuno-compromised people. *E. coli* colonise the gastrointestinal tract of infants just after birth and is the predominant throughout lives. The bacterium is responsible for a variety of diseases like gastroenteritis, urinary tract infections, and meningitis. Infections due to pathogenic *E. coli* may be limited to the mucosal surfaces or can disseminate throughout the body.

5.2.2.1 Enterotoxigenic *E. coli*

Enterotoxigenic *E. coli* is the most common diarrheal agent among the six recognized pathovars of DEC, particularly in the developing world. produces at least one member of two defined groups of enterotoxins: ST (heat-stable enterotoxin) and heat-labile enterotoxin and colonization factors which allow the organisms to colonize the small intestine causes diarrhea in infants as well as adult human beings (Qadri et al. 2005).

The heat labile enterotoxin is oligomeric toxin which resembles in structure and function to the cholera enterotoxin of *Vibrio cholerae*. The toxin exists in two forms, namely. LT-I is pathogenic for both humans and animals. LT-II has only been found in ETEC strains infecting animals. LT-I consists of one A subunit and five identical B subunits (Nagy and Fekete 2005). After the colonization of the small intestine by the LTB subunits bind to ganglioside GM1, and the A subunit activates for the enzymatic activity of the toxin by activating adenylate cyclase which results in increases in cyclic adenosine monophosphate concentrations. This inhibits neutral sodium chloride in the villus tips and stimulates chloride secretion in the crypt cells thereby resulting in osmotic diarrhea (Nataro and Kaper 1998; Kaper et al. 2004).

Heat stable enterotoxin (ST) is small, monomeric toxin in comparison to LT. Heat stable enterotoxin can be categorised into two groups: STa (or STI) and STb (or STII). STa is produced by ETEC strains infecting both humans and animals whereas STb is primarily associated with disease in animals, and not oftenly human disease (Nataro and Kaper 1998). The receptor for the ST toxins is guanylate cyclase in the small intestine. Binding to the receptor results in increased intracellular cyclic guanylate monophosphate levels which stimulate chloride secretion and inhibit NaCl absorption, resulting in subsequent net intestinal fluid secretion leading to diarrhea (Qadri et al. 2005). ETEC has great importance for developing countries due to its association with surface and potable water borne diarrheal disease outbreaks.

5.2.2.2 Enterohemorrhagic *E. coli*

Enterohemorrhagic *E. coli*, Verotoxin producing *E. coli* or Shiga-toxin producing *E. coli* are the synonyms for the same group of organism. Infections in humans can result in bloody diarrhea and hemorrhagic colitis (Nataro and Kaper 1998). In severe infections the hemorrhagic colitis progresses to hemolytic uremic syndrome, an important cause of acute renal failure in children and morbidity and mortality in adults (fatality rate in elders: 50 %). *E. coli* O157:H7 has been recognized as the most commonly occurring member of this group. Infections in humans can be acquired by direct contact with animal carriers, their feces, ingestion of undercooked ground beef and contaminated water, vegetables and fruits. The low infectious dose (1–100 CFU) enhances the risk of occurrence of disease (Paton and Paton 1998; Sharma 2006).

The pathogenicity of is determined by pathogenic factors. The most important factors are the phage-encoded Shiga toxins (stx) elements on the chromosome which inhibit protein synthesis (Nataro and Kaper 1998). Shiga toxin contains two major toxins, called Stx1 and Stx2, which share approximately 55 % amino acid homology, these are similar to the one produced by *Shigella dysenteriae* serotype 1, Nakao and Takeda (2000) and Gourmelon et al. (2006). Epidemiological studies have revealed that Stx2 is 1000 times more cytotoxic than Stx1 towards human renal endothelial cells. Isolates producing Stx2 are more associated with serious diseases than isolates producing Stx1 or Stx1 and Stx2 (Louise et al. 1995; Boerlin et al. 1999; Paton and Paton 1998). The pathogen enters the human body through contaminated food or water. The ability of bacterium to survive at lower pH (up to 2–3) facilitates survival through the acidic condition of the stomach. In the colon, the virulence genes are turned on by environmental signals. Secretion of Shiga toxins leads to local damage blood vessels in the colon result in bloody diarrhea. Absorbance of sufficient Stx in circulation causes damaging and impaired function of vascular endothelial sites. The kidneys and central nervous system are frequently affected, and hemolytic uremic syndrome may develop (Gyles 2007).

Environmental reservoirs are the potential sources of pathogenic *E. coli.* These are ideal habitat for survival, growth, and proliferation of *E. coli* as they are rich in nutrients. A wide range of different animals harbor pathogenic *E. coli*, which are consistently associated with human and animal diarrheal infection (Chapman et al. 1994). Infected cattle typically excrete ($>10^3$ CFU/g of feces) pathogenic *E. coli* (Robinson et al. 2004; Topping et al. 2008). These discharges may be released directly into the aquatic environment or indirectly through storm water runoff. The surface water carries a number of pathogenic bacteria when used for the drinking and bathing purposes. Apart from these, the water is treated in municipal treatment plants and supplied through pipelines for drinking purposes. The processed clean water sometimes also gets contaminated due to leakage of nearby sewer lines (Ram et al. 2008a).

E. coli can also survive in estuarine sediment environments (Brettar and Hofle 1992). Two highly prevalent diarrheagenic *E. coli* variants have been reported in surface and potable waters as well as in macrophytes in India. The multiple antibiotic resistant Enterotoxigenic *E. coli* (ETEC) and Shiga toxin producing *E. coli* have been reported in surface waters of river Ganga and its tributaries Gomti and Saryu (Ram et al. 2007, 2008a, b, c). Potentially pathogenic isolates of *Escherichia coli* serotype O157:H7 have been isolated from the Ganges river near Varanasi (Hamner et al. 2007).

5.3 Conventional Methods for Pathogen Detection

The detection of *Salmonellae* faces several challenges, such as the low concentration of target bacteria in foods, high amount of other bacteria and inhibitory components in samples.

5.3.1 Culture Based Methods

The traditional confirmation and identification of *Salmonella* spp. are usually based on the colony appearance on chromogenic and other selective agar media, followed by confirmation using classical biochemical and serological testing. The biochemical tests include fermentation of glucose, negative urease reaction, lysine decarboxylase activity and H_2S production. In the European Union, the reference detection methods are published by the International Organization for Standardization. The procedure for the detection of food borne *Salmonella* includes non-selective enrichment in buffered peptone water broth for 16–20 h followed by selective enrichment cultivation in selective media and incubation on two different selective agar plates for isolation of colonies. The colonies are then identified by means of biochemical tests. This procedure takes at least 72 h to complete. In Bacteriological Analytical Manual, published from the United States, the procedure for the detection of *Salmonella* includes non-selective enrichment in nutrient broth for 16 h and followed by 16 h selective enrichment cultivation in either Rappaport–Vassiliadis or tetrathionate brilliant green broth (Andrews and Hammack 2007). The colonies are isolated by using selective agar plates and identified biochemically.

The traditional method of detection of enterotoxigenic *E. coli* involves cultivation of bacteria in selective media. This includes the cultivation in MacConkey or Eosin Methylene Blue (EMB) agar followed by overnight incubation. The characteristic colonies are typical pink to red color for *E. coli*. Further confirmation is done by Indole, Methyl red, Voges-Proskauer and Citrate test which examine the ability to produce indole and sufficient acid to change the color of a methyl red indicator (Todar 2008). These assays are laborious and time consuming.

The identification of enterohemorrhagic *E. coli* in accurate manner is still a major issue. The inability of most *E. coli* O157 to ferment sorbitol is exploited in sorbitol McConkey agar. The Inernational Odranisation for Standardisation protocol (ISO 16654) recommends addition of Cefixime and potassium tellurite to sorbitol McConkey agar may increase the selectivity in samples. *E. coli* O157 generally produces colourless colonies when cultured on this media, thus distinguishing it from other enterohemorrhagic *E. coli* serogroups.

5.3.2 Immunoassays

In general, the immunoassays use antisera for detection of flagellar (H) and somatic (O) antigens. Isolates with a typical biochemical profile, which agglutinate with both H and O antisera, are identified as *Salmonella* spp. Cudjoe et al. (1995), Valdivieso et al. (2001), and Magliulo et al. (2007). Further, the positive isolates are often confirmed by serotyping and using techniques such a phage typing and pulsed-field gel electrophoresis. The immunoassays are capable of detecting 10^4–10^6 cells of *Salmonella* in foods per assay. The antibodies may cross-react with antigens in closely related bacteria, while showing low reactivity with some *Salmonella* serotypes.

Enzyme Linked Immunosorbent Assay has been widely used for detection of heat labile toxin using microtiter ganglioside methods. It requires culturing of the bacteria before testing for presence of enterotoxins. Although, the immunoassays, based upon the antigen-antibody interactions are established techniques, they often lack specificity. Serotyping has also been used to identify and characterize enterotoxigenic *E. coli* strains. The ETEC has more than 78 O groups and 34 H groups identified; therefore the determination of O serogroups associated with the lipopolysaccharides in the cell wall and H serogroups of the flagella is difficult (Qadri et al. 2005). A huge number of combinations of O and H groups make serotyping less suitable for identification of enterotoxigenic *E. coli*.

Enterohemorrhagic *E. coli* O157:H7 colonies are confirmed with biochemical tests and immunoassays having the O157 somatic antigen and H7 flagellar antigen. A variety of tests including enzyme-linked immunosorbent assays, agglutination, immunoblotting or Vero cell assay can be used to detect the verocytotoxin.

5.3.3 DNA Amplification Method

Polymerase Chain Reaction, a molecular technique has been used most frequently for the detection of *Salmonella* (Malorny et al. 2007; Chen et al. 2010; O'Regan et al. 2008; McGuinness et al. 2009; Jyoti et al. 2010). The virulence *invA* gene has been extensively used for the detection of *Salmonella* in water and food. Most of these methods which are in routine use provide results in approximately 24 h.

PCR can be used for differentiating diarrheagenic strains from nonpathogenic strains in both clinical and environmental samples (Sjöling et al. 2007). This approach to ETEC detection relies on the presence of the genes encoding heat labile and/or heat stable enterotoxins. The *E. coli* O157:H7 specific virulent genes such as *stx1* and *stx2* are used for the reliable and accurate detection (Ram et al. 2011).

5.3.4 Real Time Polymerase Chain Reaction

Real Time PCR, a recent advancement in PCR technology simultaneously amplifies and detects target DNA in samples. It uses fluorescent detection strategies for the quantification of nucleic acid in a reaction without post-PCR processing. With the addition of an optical module, real time PCR allows the capture of fluorescent signals from amplified PCR products. Computer software records and displays the amount of fluorescence in relative fluorescence units (RFU). The amplification cycle at which the fluorescence exceeds the cutoff level is known as threshold cycle (C_T) Corless et al. (2000). This threshold is calculated as a function of the amount of background fluorescence and is plotted at a point in which the signal generated from a sample is significantly greater than background fluorescence (Kubista et al. 2006; Espy et al. 2006). With increasing concentration of target DNA, the threshold of the sample fluorescence will be achieved earlier. The amount of initial copy number of the target in unknown sample can be calculated by comparing the C_T obtained of that sample with a standard curve, generated from serial dilutions of a known amount of the target DNA (Ibekwe et al. 2002).

One of the major probe chemistries is Molecular Beacon (MB) probe, which is widely used for the detection of target nucleic acids in samples. It is a short single-stranded oligonucleotide molecule that forms a hairpin with a loop and stem. The loop is designed to hybridize to a 15–20 nucleotide fragments of the target DNA sequence while the stems are composed of five to seven self complementary nucleotides. A fluorescent reporter molecule is attached at the 5′- end of the molecular beacon and a dark quencher at 3′- end. In the native state, the MB is closed and both the reporter and quencher are in close proximity of each other. The signal released by reporter is masked by the quencher. During annealing step of PCR, the binding of molecular beacon to its target leads to increased fluorescence, due to separation of reporter and quencher, which directly corresponds to accumulation of product (Fig. 5.2) (Kubista et al. 2006).

The possibility of cross-contamination between analyses is reduced due to closed tube format, and provides rapid, continuous data collection and reduction in time required to obtain results. These salient features have made real time PCR a potential alternative to conventional culture-based or immunoassay-based testing methods used for diagnosing infectious diseases.

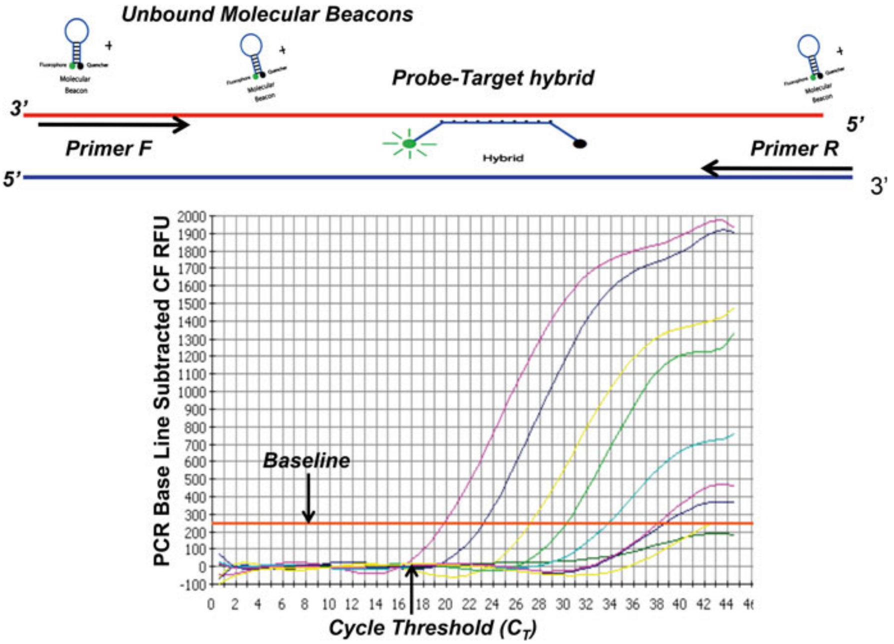

Fig. 5.2 Mechanism of target binding of molecular beacon probe (*above*). As a result of target hybridization the Cycle Threshold (C_T) is generated (*below*)

5.4 Gold Nanoparticle Probes for Detection of DNA

Currently, nano-biotechnology is evolving with the simultaneous developments in nanoscience, biology and medicine. The potential applications of nanotechnology are becoming increasingly important for the development of ultrasensitive DNA detection systems. Organic fluorophores have been used to achieve the recognition of different targets. These fluorophores often suffer from quenching and limited multiplexing. Apart from these, the need of expensive instrumentation makes them unsuitable for point-of-care diagnostics. Gold nanoparticles possessing unique and outstanding optical properties have been explored for bio-diagnostics (Storhoff et al. 2004; Sato et al. 2007). GNP-based DNA detection has high sensitivity as compared to conventional fluorescence based assays due to the extremely its high molar absorptivity of (approximately 1000 times higher than that of organic dyes) (Zhao et al. 2008).

The optical properties of gold nanoparticles are governed by collective oscillation of electrons at surfaces known as surface plasmon resonance. The Gold nanoparticles have a high surface to volume ratio, therefore the surface electrons are sensitive to change in the dielectric (refractive index) of the medium. Any changes to the environment of these particles including surface modification, aggregation and medium refractive index lead to colorimetric changes of the dispersions (Rosi and Mirkin 2005). The aggregation behaviour of Gold nanoparticles has been widely explored for different applications. This has further facilitated the application in bio-detection via numerous detection methods (Boyer et al. 2002; Niemeyer 2001). Due to its outstanding conjugation ability various analytes such as nucleic acids, sugars, proteins via the strong affinity of gold surface with thiol Ligands can bind for target detection (Schofield et al. 2007).

The colloidal solution of gold nanoparticles is monodisperse red and exhibit a narrow surface plasmon absorption band centered on 520 nm (depends upon particle size) in the UV-Visible spectrum. The colorimetric change pointed to a simple and inexpensive way of diagnosing disease, suggested that assays based upon such nanostructures should have higher selectivities than the conventional molecular fluorophore-labeled structures. The properties and application of gold nanoparticles in nano-diagnostics have received a lot of attention for the detection of DNA, using the well-known chemistry of thiol adsorption to gold.

5.4.1 Principle

5.4.1.1 Gold Nanoparticles Probes for DNA Detection

The Gold nanoparticles are bio-functionalized with the thiol modified single stranded DNA (ssDNA) to generate probe for DNA detection (Lu and Liu 2006). The computational exercises for the selection of ssDNA probe strand are done to create a complementarity with target of interest. Gold nanoparticles are conjugated with the synthesized ssDNA having thiol group. After hybridization with the target, the probes come in the close proximity, which leads to change in color. As a result, the particles aggregate and the solution appear purple/blue, corresponding to a characteristic red shift in the surface plasmon resonance towards higher wavelength (Storhoff et al. 2004). A number of factors viz. size and shape of the nanoparticle, refractive index of the surrounding media and inter-particle distance are taken into account for use in colorimetric detection of DNA (Baptista et al. 2008). The Gold nanoparticles obtained by citrate-reduction present in solution are charged particles and they are sensitive to changes in solution dielectrics. Hence, with the addition of NaCl the surface charge is shielded leading to a decrease in inter-particle distance and particle aggregation.

Mirkin and co-workers reported the colorimetric detection of DNA targets based on the cross-linking mechanism use of Gold nanoparticles probes. Two different batches of ssDNA are designed to detect target DNA. During hybridization, a polymeric network of Gold nanoparticles probes is generated due to aggregation, turning the solution from red to blue (Mirkin et al. 1996). This aggregation process is slower and capable to detect smaller targets (Sato et al. 2003).

Another mechanism of analyte detection has been well demonstrated by Sato and coworkers. The thiol modified single stranded DNA can be immobilized on Gold nanoparticles. With the addition of Gold nanoparticles probes aggregate together and detect the target DNA. As a result, there is significant change in colour of the solution from red to blue (Sato et al. 2007).

The basic steps of DNA detection using gold nanoparticle probes include (Fig. 5.3):

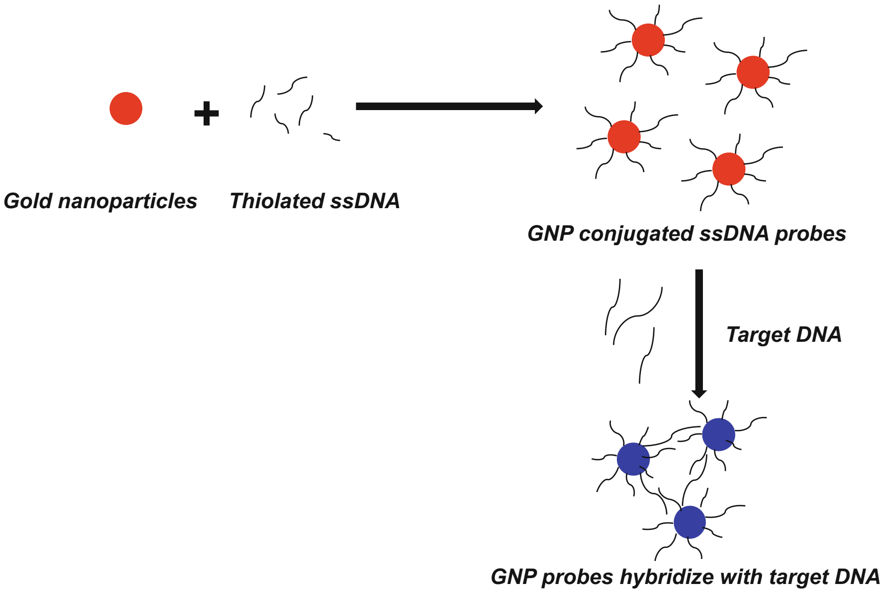

Fig. 5.3 Schematic representation of synthesis of Gold nanoparticle probes and target DNA detection

1. Synthesis of Gold Nanoparticles: Gold nanoparticles are synthesized using citrate reduction method (Pandey et al. 2008). Aqueous solution of Hydrogen tetrachloroaurate (1 mM $HAuCl_4$) is brought to the boiling with stirring in a round bottomed flask fitted with a reflux condenser. Trisodium citrate solution is added rapidly when the solution begins to reflux. The solution is further boiled for another 15 min. In due course, the colour of the solution is changed from pale yellow to deep red. This red solution is allowed to cool at room temperature with continuous stirring.
2. Functionalization of gold nanoparticles with thiol-modified DNA: The single stranded oligonucleotides (complementary to some parts of target) are used for synthesizing probes by immobilizing onto the gold nanoparticles. These oligonucleotides are modified with thiol group (-SH) at their 5′/3′-ends. The single stranded DNA (ssDNA) stabilized Gold nanoparticles are prepared by the method with slight modification reported previously (Lu and Liu 2006). The gold nanoparticles (selected size ~20 ± 0.2 nm diameter) are incubated with different batches (number varies with the target size) of thiol modified ssDNAs separately. The solution is buffered with the Tris-acetate and salt. After this the unbound ssDNA is removed by centrifuging the solution. The ssDNA grafted Gold nanoparticles is resuspended in buffer and room temperature. The absorption spectra of the bio-functionalized Gold nanoparticles are recorded in UV-visible spectroscopy.
3. Hybridization of Gold nanoparticles probes with targets and detection: The synthesized Gold nanoparticles probes are allowed to hybridize with the target DNA under controlled conditions. The hybridization mixture includes target DNA, Gold nanoparticles probes and monovalent salt. Hybridization and target detection is examined for change in solution colour by naked eye and the change in surface Plasmon resonance band is recorded in UV-visible spectroscopy. The reduction in interparticle distances and aggregate formation is observed in Transmission Electron Microscopy.

5.5 Aptamers for Pathogen Detection

Aptamer is single-stranded nucleic acid (DNA or RNA) that usually possesses high affinity and results in a significant conformation change upon binding with a wide range of targets. Aptamers are generally selected from the pools containing randomly created sequences through an in vitro systematic evolution of ligands by exponential enrichment (SELEX). Compared to antibody-based biosensors, aptamer-based biosensors (aptasensor) possess unprecedented advantages with high productivity, affinity, selectivity, and stability (Zhou et al. 2014).

Aptamers, with appropriate secondary structures that function as ligands, are emerging as new analytical reagents, which can be coupled with different transduction systems. Possibly, the most important advantages of aptamers from an analytical point of view are the high affinity and binding specificity for their targets, ease to be labeled with different reporter molecules, and their relatively low production cost, which make them ideal reagents for the development of sensors. Although aptamer applications are dominated by clinical or medical diagnostics market so far, first steps have already been taken for the application of aptamers to ensure food safety.

Several bacterial aptamers had been isolated and recently used in identification of bacteria, including *Escherichia coli*, *Mycobacterium tuberculosis*, *Salmonella enterica* and *Bacillus anthracis* (Maeng et al. 2012).

Gold nanoparticles are gold particles that range in size from 1 nm to several hundred nanometers and possess strong light scattering properties. The intensity of light scattering is based on the size of the particle. Moreover, Gold nanoparticles can be easily conjugated with protein or modified DNA molecules through sulfhydryl linkages. These properties make Gold nanoparticles a useful tool for ultrasensitive molecular detection (Jyoti et al. 2011). Moreover, a GNP-based amplification method has been developed and the system was shown to be capable of detecting prostate-specific antigen with sensitivity in the attomolar range.

5.5.1 Advantages of Aptamers Over Antibodies

Principally, biosensor consists of a biological recognition component and a signaling component. The recognition element detects the target molecule while that the signaling component converts the biological recognition into detectable signals. The specificity, binding affinity and sensitivity of recognition molecules are the utmost important for biosensors performance. A number of recognition molecules have been used including the antibodies due to varying reasons. Inspite of different applications and uses, antibodies face certain lacunae. Being proteinacious in nature, the antibodies are highly sensitive towards temperature variations. The specificity and binding with the target also faces variations. The irreproducibility of results due to instability makes it difficult for working with antibodies. Therefore, it is highly desirable for potential alternative ligands as a new platform for diagnosis. DNA Aptamers are attractive for biosensor development due to their small size, high stability, high binding affinity and specificity, and ease of modification.

5.5.2 Detection of Whole Bacteria

Detection of target bacteria as an analyte will be a major breakthrough. This will remove the steps involved in isolation of genomic DNA and amplification of PCR product. Aptamers have also been involved in developing lateral flow assays for the direct detection of bacterial pathogens. Such aptamers are developed using Systematic Evolution of Ligands by Exponential Enrichment technique. In this approach, one of the aptamer specific to the analyte is immobilised on the nitro cellulose membrane as test line directly or through biotin–avidin interaction. Another aptamer is conjugated to colloidal nanoparticles. The bacterial pathogen (analyte) is put on the sample pad which interacts with the nanoparticle conjugated aptamer. As the complex moves along the strip, the aptamer immobilised at test line will also interact with the bacterial pathogen to form a sandwich and the gold nanoparticles get captured at the test line producing a red colour.

5.5.3 Method

1. Synthesis of Aptamer conjugated Gold Nanoparticle probes: The single stranded aptamers are used for synthesizing probes by immobilizing onto the gold nanoparticles. The aptamers are modified with thiol group (-SH) preferably at their 5′-ends. The gold nanoparticles are incubated with thiol modified aptamers. The final concentration of aptamers is 2 μM. The solution is incubated with the Tris-acetate and NaCl. The unbound thiolated aptamers are removed by washing. This is followed by resuspension of aptamers-conjugated GNP at room temperature for further characterization.
2. Colorimetric detection of target bacteria using Aptamer-conjugated Gold Nanoparticle probes: Different concentrations of target bacteria are added to the aptamer-conjugated Gold nanoparticles solution. After incubation the monosodium salt (NaCl) is introduced to the mixtures, followed by UV–vis characterization.

5.6 Development of Nanoaptasensors Pathogen Detection

5.6.1 Strip Based Lateral Flow Device

Strip assays are extremely versatile and are available for an enormous range of analytes including mycotoxins, blood proteins and bacterial pathogens. Lateral flow assays are essentially immunoassays adapted to operate along a single axis to suit the test strip format. There are a number of variations of the technology that have been developed into commercial products for detection of bacterial pathogens (Singh et al. 2015).

5.6.2 Working of Lateral Flow Assay (Fig. 5.4)

A lateral flow rapid test strip consists of the following components:

Sample pad- It is an adsorbent pad onto which the test sample is applied.

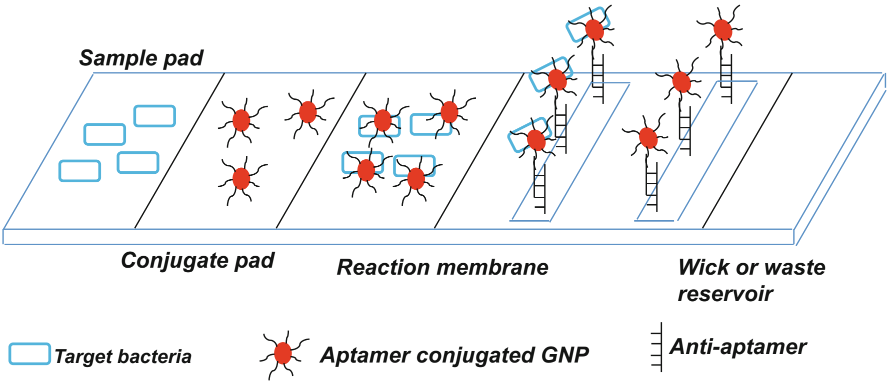

Fig. 5.4 Schematic representation of strip based lateral flow device

Conjugate pad- It contains aptamers conjugated gold nanoparticles specific to the target pathogen.

Reaction membrane- A nitrocellulose membrane onto which anti-target aptamers are immobilized in a line that crosses the membrane to act as a capture zone or test line. This is followed by a control zone which contains oligonucleotides complementary to the aptamer.

Wick or waste reservoir- Another absorbent pad designed to draw the sample across the reaction membrane by capillary action and collect it.

The components of the strip are usually fixed to an inert backing material and may be presented in a simple dipstick format or within a plastic casing with a sample port and reaction window showing the capture and control zones.

5.7 Challenges of Aptamer-Based Biosensors

Although, a number of aptamers are being used for sensing the pathogens and these have potentials to replace existing technologies in near future, a number of challenges can be faced. The lack of high quality DNA aptamers for many important targets, such as bacterial pathogens, glucose and many others is the foremost challenge. Most of the aptamers in use lack characterization, which makes it difficult for practical utility. The main challenge lies in the target detection in a complex sample matrix.

5.8 Conclusion

The present scenario of over population, urban crowding and stressed rural–urban interfaces in developing nations has created an urgent need to develop an ideal detection system which overcomes drawbacks in existing methods for detection of water-borne pathogens and risk assessment. Various conventional and analytical methods exist to detect bacterial pathogens in different matrices including environmental and clinical settings. Very often they suffer from limitations such as poor sensitivity, selected specificity, time consuming costly instrumentations, trained personnel etc. The detection system or device needs to be based on simple, rapid, highly sensitive and specific methodology for detection of pathogens in a single assay. Aptamers have been shown to be versatile and effective as molecular probes for molecular recognition. Since *E. coli* and *Salmonella* are major prevalent organisms in water, there exists a scope for developing such rapid and simple strip based detection system. With the deteriorating water quality in the developing countries and looking at the occurrence of water borne infections, it becomes indispensable to have some point-of-care diagnostic system for water quality assessment.

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Chapter 6
Nanotechnology in Food Packaging

Bambang Kuswandi

Abstract Nanotechnology promises many interesting changes for better life. Nanotechnology can be used to improve health, wealth, products and quality of life. Food nanopackaging is still a rather unexplored field of nanoscience and food science. Here I review developments in nano-packaging. This chapter describes first biobased food packaging for biodegradable packaging. Biobased packaging is indeed an alternative to conventional packaging with non-degradable plastic polymers that are a threat to the environment. Biobased packaging reduces waste, extend the shelf life, and enhance food quality. The next section discusses nanomaterials that improve packaging, such as better barrier properties, mechanical strength, flexibility and stability. Active packaging refers to the use of active materials such as antimicrobials and oxygen scavenging reagents. Smart packaging is the use of nanosensors and nanodevices that detect freshness or contaminants in foods or monitor changes in packaging conditions or integrity. The last section discusses safety issues and heath concerns of nanopackaging.

Keywords Nanotechnology • Food packaging • Sensors • Nanocomposites • Nanoparticles

6.1 Introduction

Nanotechnology involves the fabrication, manipulation and characterization of structures, devices or materials at the nano size, approximately 1–100 nm in length, that have at least one dimension. When particle size of material is reduced into nano size, the resulting material exhibits physical and chemical properties that are significantly different from the properties of macroscale materials composed of the same substance. Therefore, it would seem illogical that structures in the size of 1–100 nm would not only exist but would also have implications and applications that could

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Fig. 6.1 Key functions of packaging systems, i.e. container of the product, preservation and protection of the product quality, presentation and identification of the product as sales element, facilitation for transportation and distribution of the product, and information of the product to the consumers

be essential to humankind (Sozer and Kokini 2009; Ravichandran 2010). Nanotechnology promises many interesting changes to improve health, wealth and quality of life, as well as reducing impact on the environmental.

Packaging systems are those products which are manufactured with any material in order to protect, to contain, to manipulate, to distribute, to transport and to identify each article along its supply chain, from raw materials to end users (Fig. 6.1). These functions are compulsory to define accurately any kind of packaging, however, according to the types of products which have to be packed and preserved, a wide range of requirements are also needed, such as mechanical, thermal and barrier properties. Due to the range of advanced functional properties of nanomaterials that can bring to packaging materials, therefore, nanomaterials are increasingly being used in the food packaging industry. It was reported that around 500 nano-packaging products are estimated to be in commercial use, while nanotechnology is predicted to be used in the manufacture of 25 % of all food packaging within the next decade (Reynolds 2007). In nano-packaging, it can also be designed to release antimicrobials, antioxidants, enzymes, flavors and nutraceuticals to extend shelf life (Cha and Chinnan 2004). The new nanotechnology products for food packaging were in the pipeline and some anti-microbial films to improve the shelf life of food and dairy products, have already been entered the market (El Amin 2005).

Novel food packaging technology is by far the most promising benefit of nanotechnology in the food industry in the near future, as described very recently by Dasgupta et al. (2015) regarding application of nanotechnology in the agro-food sector, as one of the fastest growing fields in nano-research. Furthermore, it showed by recent research trends in food processing, packaging, nutraceutical delivery, quality control and functional food. In this field many organizations, scientists, inventors as well as industries are coming up with new techniques, protocols and products that have a direct application of nanotechnology in agriculture and food products (Dasgupta et al. 2015). In food packaging, by applying nanotechnology, companies are already producing packaging materials that are extending the life of food and drinks and improving food safety. Food packaging and monitoring are major focus of food industry–related nanotechology research and development (Brody 2003). The leading development in food packaging is active and smart packaging that promises to improve food safety and quality and optimizes product shelf life (Kuswandi et al. 2011). In active and smart packaging, many companies and universities are developing packaging that would be able to alert if the packaged food becomes contaminated, respond to a change in environmental conditions, and self-repair holes and tears.

Currently in packaging industries, the largest part of materials used is non-degradable petroleum based plastic polymer materials. As a result, this non-degradable food packaging materials, represent a serious problem on the global environmental (Kirwan and Strawbridge 2003). Therefore, the use of bio-based packaging materials, such as edible and biodegradable films from renewable resources (Tharanathan 2003), could at least to some extent solve the waste problem by reducing packaging waste and also extend the shelf life, which in turn, enhance food quality. In this respect, by means of the correct selection of materials and packaging technologies, it is possible to keep the product quality and freshness during the time required for its commercialization and consumption (Stewart et al. 2002; Kuswandi et al. 2011).

However, the use of bio-based materials for food packaging has been very limited currently. This is due to natural polymers have the poor barrier and weak mechanical properties. Therefore, these natural polymers were frequently blended with other synthetic polymers or chemically modified with the goal of extending their applications in packaging (Petersen et al. 1999). In addition, like conventional packaging, bio-based packaging must serve a number of important functions, such as containment and protection of food, maintaining its sensory quality and safety, and communicating information to consumers (Robertson 1993). Other nanotechnology that could help to reduce waste of the packaging associated with processed foods is the application of nanocomposites in packaging. The application of nanocomposites promises to enhance the use of edible and biodegradable films in packaging (Lagaron et al. 2005; Sinha Ray and Bousmina 2005) and will support the preservation of fresh foods, which in turn, extending their shelf life (Vermeiren et al. 1999).

Nanotechnology was used to create tiny particles in the film, to improve the transportation of some gases through the plastic films to pump out unwanted carbon dioxide that would shorten the shelf life of the foods. In addition, they are also looking at whether the film could also provide barrier protection and prevent gases such as oxygen and ethylene from deteriorating foods (Silvestre et al. 2011; Duncan 2011). Nowadays, numerous food and pharmacy researchers are working to applied

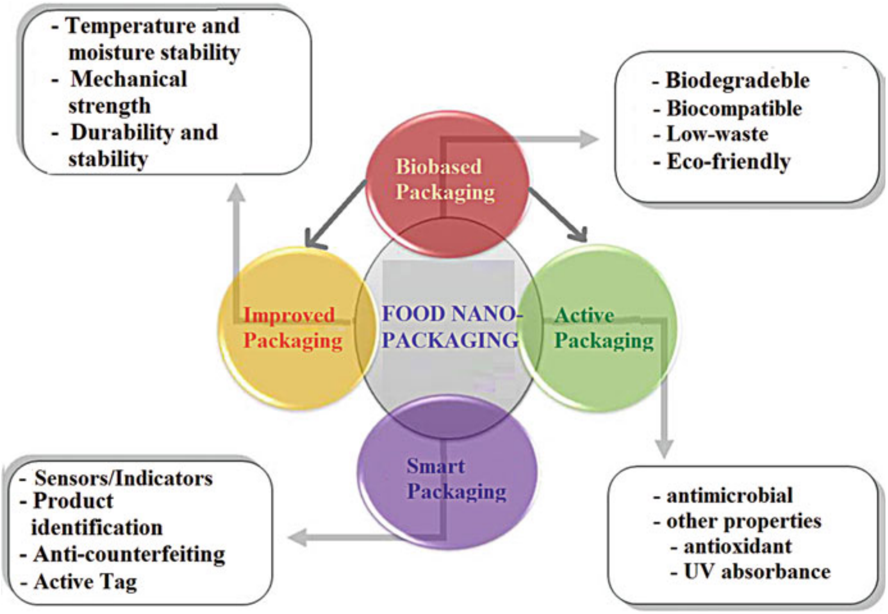

Fig. 6.2 Food nano-packaging, classification, functions and features, including: bio-based packaging for biodegradable, biocompatible, low-waste and eco-friendly; improved packaging in term of mechanical strength, durability and flexibility, and temperature and moisture stability; active packaging based nanocomposites as active material, e.g. antimicrobial and other properties, e.g. antioxidant, UV absorbance etc.; and smart packaging with nanosensors as intelligent function in packaging for the detection of food relevant analytes (gasses and small organic molecules), active tag and product identification and anticounterfeiting. Biobased packaging can also be used in improved and active packaging

nanotechnology with the aim to improve delivery of medicines, vitamins or fragile micronutrients in the daily foods by creating tiny edible capsules based nanoparticles that release their contents on demand at targeted spots in the body. Therefore, it will provide significant health benefits, such as reduced risk of heart attack, stroke, neurodegenerative diseases and cancer (Koo et al. 2005; Yan and Gilbert 2004). In addition, nanoparticles may be used to introduce multiple functionalities like color and odors but also to act as reservoirs for the controlled release functions of drugs or fungicides (Lee et al. 2003). Although promising results were obtained, the road to successful bio-nanocomposites is still long development (Sorrentino et al. 2007).

Despite a tremendous growth in this field, food packaging nanotechnology is still rare subfield of the nanotechnology spectrum as well as in the food science and technology. This article addresses to fill this knowledge shortage by providing a comprehensive review of current developments in nano-packaging technology as it applies to foods and food-related systems, focusing specifically on applications which are most likely to enjoy consumer acceptance and regulatory attention in the immediate future as given in Fig. 6.2. Covered topics include bio-based packaging for biodegradable packaging for environmental concern; improved packaging for improved barrier properties, mechanical strength and flexibility as well as stability; active packaging for antimicrobials, and oxygen scavenging; smart packaging for intelligent functions, such as sensors/indicators that detect freshness or contaminants in foods or monitor changes in packaging conditions or integrity. Safety issues on specific health concerns related to these various applications are also briefly discussed. The article concludes with a brief overview of the outlook of the nanopackaging materials in the future.

6.2 Biobased Packaging

Biobased packaging is biodegradable packaging films that are applied to food products to control moisture transfer and/or gas exchange in order to improve safety and preserve the nutritional and sensory quality (Siracusa et al. 2008). These packaging materials are perceived to be more environmental friendly than the other conventional packaging films. Like any kind of packaging, bio-based packaging provides a barrier between a food product and its environment, thereby protecting it against unwanted effects of microorganisms, ambient relative humidity and gas conditions. The specific characteristic that distinguishes biodegradable packaging films from other packaging solutions is that they are capable of decaying through the action of living organisms (Del Nobile et al. 2009). This packaging type is generally perceived to be more environmental friendly as the breakdown products are all completely natural, i.e. carbon dioxide, biomass and water. Bio-based packaging does not (or less) use fossil fuels to produce the materials, but uses renewable sources, upon disposal energy can be recovered by incineration.

Commonly, biodegradable plastics that used as materials in bio-based packaging, are polymeric materials in which at least one step in the degradation process via naturally occurring organism's metabolism. Under appropriate conditions of moisture, temperature and oxygen availability, this biodegradation leads to fragmentation or disintegration of the plastics with no toxic or environmentally harmful residue (Chandra and Rustgi 1998). These biodegradable polymers can be classified according to their source: (i) Polymers directly extracted from biomass, such as polysaccharides, proteins, polypeptides, polynucleotides. (ii) Polymers produced by chemical synthesis of bio-based monomers or mixed biomass and petroleum, such as polylactic acid or bio-polyester. (iii) Polymers produced by micro-organism or genetically modified bacteria, such as polyhydroxybutyrate, bacterial cellulose, xanthan, curdian and pullan.

The success concept of bio-based nanocomposite in the area of synthetic polymers has stimulated new research on nanocomposites based on biodegradable polymers for food packaging applications (Sorrentino et al. 2007). Description of biopolymers is available in literature (Kaplan 1998; Doi and Steinbuechel 2002; Steinbuchel 2003; Mohanty et al. 2005; Sorrentino et al. 2007). The problems associated with biodegradable polymers are performance, processing, and cost. This is due to "performance and processing" are common to all biodegradable polymers in

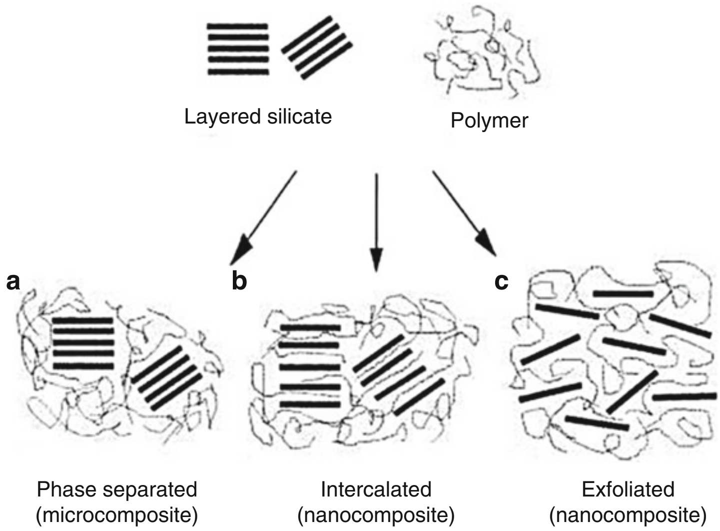

Fig. 6.3 Three types of composites when layered clays are incorporated with the polymer: (**a**) tactoid, phase-separated microcomposite; (**b**) intercalated nanocomposite and (**c**) exfoliated, polymer–clay nanocomposite (Courtesy of Alexandre and Dubois 2000)

spite of their origin (Trznadel 1995; Scott 2000). The problem particularly, brittleness, low heat distortion temperature, high gas and vapor permeability, poor resistance to protracted processing operations have strongly limited their applications. The application of nanotechnology to these polymers could open new possibilities for improving both the properties and the cost-price-efficiency.

Three main types of composites can be formed when the layered clay is incorporated with a polymer, as given in Fig. 6.3 (Alexandre and Dubois 2000). Types of composites formed mostly depend on the nature of the components used (i.e. layered silicate, organic cation and polymer matrix) and the method of preparation. Micro-composites are formed when the polymer chain is unable to intercalate into the silicate layer, which therefore phase separated polymer/clay composites are formed as shown in Fig. 6.3a. Intercalated nano-composite is obtained when the polymer chain is inserted between clay layers such that the interlayer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other as shown in Fig. 6.3b. Exfoliated nano-composites are formed when the layers of the clay have been completely separated and the individual layers are distributed throughout the polymeric matrix as shown in Fig. 6.3c.

Due to nanometer-size particles obtained by dispersion, these bio-nanocomposites can remarkably improved mechanical, thermal, barrier and physico-chemical properties, when compared with the starting polymers and microscale composites. As an example, it shows great promise in providing excellent barrier properties, due to the presence of the clay layers able to delay the molecule pathway making the diffusive path more tortuous (Bharadwaj 2001). In addition, the preparation and characterization of various kinds of biodegradable polymer nanocomposites showing properties

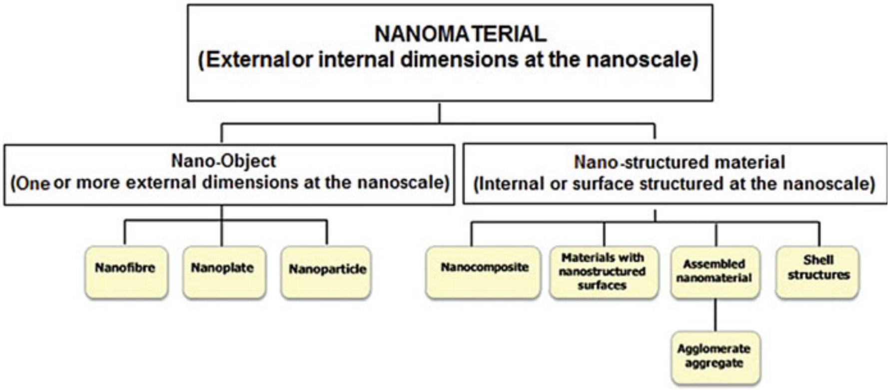

Fig. 6.4 Terminology of nanomaterial used in nano-packaging: (**a**) nano-object, and (**b**) nano-structured material. Nano-object consist of nanofibre, nanoplate and nanoparticle, while nano-structured material consist of nanocomposite, material with nanostructured surfaces, assembled nanomaterial and shell structure

suitable for a wide range of applications (Sinha Ray and Bousmina 2005). Currently, the most studied bio-nanocomposites suitable for packaging applications are starch and derivates, i.e. polylactic acid, poly(butylene succinate), polyhydroxybutyrate, and aliphatic polyester. Thus, bio-based packaging can also be used for improved packaging and active packaging.

In general, the application of the nanotechnology in polymer based packaging that used nanoparticles can be divided into two categories: (i) nano-object materials (materials with nanoscale dimensions less than 100 nm) and (ii) nano-structured materials as shown in Fig. 6.4. In nano-objects, mostly nanomaterials used as a filler (nano-reinforcement), which involves the use of nanoplate, nanoparticles and nanofibers (such as metal oxides nanoparticles, nanoclays, carbon nanotubes and other fillers like metallic nanoparticles). While in nano-structured materials, the nanomaterials are dispersed into a polymer matrix as nanocomposites.

Actually, the applications of nanomaterial materials in packaging are developed mainly into three applications: (i) improved packaging, such as barrier performance pertaining to gases such as oxygen, carbon dioxide, and ultraviolet rays, as well as to add strength, stiffness, dimensional stability, and heat resistance; (ii) active packaging, such as antimicrobial or other properties (e.g. antioxidant, UV absorbance) with intentional release into- and consequent effect on the packaged food in term of taste, freshness and self life; (ii) smart/intelligent packaging, such as oxygen indicators, freshness indicators and pathogen. The three main applications of nanomaterial in food packaging was also described as the research trends of food packaging with the help of nanotechnology (Ranjan et al. 2014), where in food packaging mainly related with nano-reinforcement, nanocomposite active packaging and nanocomposite smart packaging. Table 6.1 gives an overview of these potential applications of the nanotechnology in food packaging. In improved packaging, the presence of nanoparticles in the polymer matrix materials improves the properties

Table 6.1 Packaging applications of nanomaterials: (a) improved packaging, (b) active packaging and (c) smart packaging

Applications	Descriptions	Key nanomaterials
Improved packaging	Incorporation of nanomaterials into the packaging to improve physical performance, durability, barrier properties, biodegradation, biocompatibility and environmental friendly	Clays, SiO2
Active packaging	Incorporation of nanomaterials with antimicrobial or other properties (e.g. antioxidant, UV absorbance) with intentional release into- and consequent effect on the packaged food in terms of taste, freshness and self life	Ag, TiO_2
Smart packaging	Incorporation of nanosensors to monitor and report on the condition of the food (e.g. oxygen indicators, freshness indicators and pathogen)	High variability

of the material. Besides barrier properties, strength, stiffness, dimensional stability and heat resistance of materials can be improved due to nanoclays or SiO_2 nanoparticles addition. In active packaging, nanoparticles as active agents are being developed specially for antimicrobial packaging applications; silver, gold and metal oxide nanoparticles are the most studied nanoparticles with antimicrobial function, with silver nanoparticles already found in several commercial applications. Moreover, they can be suitable for other active packaging fields such as ethylene removers. In intelligent packaging, nanoparticles can be applied as reactive particles in packaging materials to inform about the state of the packaged product. The so-called nanosensors are able to respond to external stimuli change in order to communicate, inform and identify the product with the aim to assure its quality and safety. The recent developments for polymer nanomaterials for smart food packaging include oxygen indicators, freshness indicators and pathogen.

6.2.1 Starch

Starch is a potential raw material and renewable source, due to its cyclic availability from many plants and excessive production related to current needs and its low cost (Smits et al. 1998; Gonera and Cornillon 2002). There are many ways to using starch as packaging material (Kim and Pometto 1994). Starch alone does not form films with appropriate mechanical properties without chemically modification or plasticized. If starch is treated in an extruder by both thermal and mechanical energy, it can be converted to a thermoplastic material. In the thermoplastic starches production, plasticizers are used to reduce intra-molecular hydrogen bonds and to provide stability to product properties. Corn is the primary source of starch for bioplastics, although more recent global research is evaluating the potential use in bioplastics for starches from potato, wheat, rice, barley, oat and soy sources.

Since its hygroscopic nature, starch-based absorbent pads are used as a potential alternative to conventional absorbent for meat exudation (Smith et al. 1995). Films based starch, could be employed as packaging for perishable foods (such as fruits and vegetables, snacks or dry products). However, in these applications, efficient mechanical, oxygen and moisture protection is needed. Thermoplastic starch (TPS) alone often cannot meet all these requirements. Due to its hydrophilicity, its performance changes during and after processing, due to changes in the water content. To overcome this drawback, the used of clay as filler have been reported as follows.

Clay, as potential filler, has been used for improving the properties of TPS in such applications (De Carvalho et al. 2001; McGlashan and Halley 2003; Wilhelm et al. 2003; Chen and Evans 2005; Yoon and Deng 2006). Starch/clay nanocomposite films have been obtained by dispersing montmorillonite nanoparticles via polymer melt processing techniques. It has been shown that both the tensile strength and the elongation at break of TPS were increased with the presence of small amounts (>5 %) of sodium montmorillonite. Furthermore, the temperature of decomposition was increased, while the relative diffusion coefficient of water vapor was decreased (Park et al. 2003). Mechanical characterization results also show an increase of modulus and tensile strength. In addition, the conformity of the resulting material samples with actual regulations and European directives on biodegradable materials was verified by migration tests (Avella et al. 2005).

6.2.2 Polylactic Acid

The conventional chemical synthesis used for the production of polymers gives a wide variety of biopolyesters. Polylactic acid is thermoplastic aliphatic polyester, biodegradable and the polymer with the highest potential for a commercial major scale production of renewable packaging materials. Polylactic acid is derived from renewable resources by means of a fermentation process using sugar from corn, followed by either ring-opening polymerization or by condensation polymerization of lactic acid. It is one of the most important biocompatible and biodegradable polymers in a group of degradable plastics. Polylactic acid represents a good candidate to produce disposable packaging due to its good mechanical properties and process ability (Murariu et al. 2008).

The properties of the polylactic acid material are highly related to the ratio between the two forms (L or D) of the lactic acid monomer. L- polylactic acid is a material with a very high melting point and high crystallinity, whereas a mixture of D- and L- polylactic acid results in an amorphous polymer with a low glass transition temperature. Although polylactic acid is an eco-friendly boiplastic with good biocompatibility, poor hardiness, slow degradation, hydrophobicity, and lack of reactive side-chain groups limit its application (Rasal et al. 2010). Therefore, the tailoring of its properties to reach end-users demands is required. In addition, mechanical properties being better than or comparable to conventional plastics, controlled surface properties such as hydrophilicity, roughness, and reactive functionalities are the successful implementation of polylactic acid as material in food packaging. Many has been reported for the preparation of polylactic acid/clay nanocomposite materials (Choi et al. 1997; Ogata et al. 1997; Bandyopadhyay et al. 1999; Pluta et al. 2002; Sinha Ray et al. 2002a, b, 2003; Chang et al. 2003; Paul et al. 2003).

The incorporation of clays in the polylactic acid to produce a polylactic acid-clay nano-composite to improve polylactic acid's mechanical and properties as well as to accelerate its degradation rate have been developed (Bandyopadhyay et al. 1999). Solvent casting of mixtures of polylactic acid and organophilic clay in chloroform resulted in materials with an enhanced crystallization tendency and increased Young's modulus (Ogata et al. 1997). However, the glass transition temperature increases only slightly with increasing clay content. This may be due to the microcomposite structure rather than nanocomposite structure. As a matter of fact, a strong tendency of tactoids formation was observed. The polylactic acid/layered silicate nanocomposites, prepared by simple melt extrusion, exhibited remarkable improvement of material properties in both solid and melt states compared to the matrix without clay (Sinha Ray et al. 2002a).

The combination of polylactic acid and clays, at the nano-scale, often results in remarkably improved mechanical and functional properties compared with pure polylactic acid or conventional composites (Okamoto et al. 2001). Different polylactic acid/silicate nano-composites have been explored: montmorillonites and fluorohectorites clays, were blended with the polylactic acid (Oliva et al. 2007; Aguzzi et al. 2007). Nanocomposites of the polylactic acid and polylactic acid/polycaprolactone blends were obtained by melt-mixing with a properly modified kaolinite (Cabedo et al. 2006). In this case, all nanocomposites showed an improvement in the gas barrier, mechanical and thermal properties with regard to the polymers and blends without clay.

6.2.3 Polyhydroxybutyrate

Polyhydrobutyrate has been the subject of extensive studies as an environmentally friendly polymeric material which is the most popular polyhydroxyalkanoate used in food-packaging. Polyhydrobutyrate is a polymer belonging to the polyesters class that are of interest as bio-derived and biodegradable plastics (Frieder 2010). Polyhydrobutyrate is produced by microorganisms (such as *Ralstonia eutrophus* or *Bacillus megaterium*) (Lenz and Marchessault 2005) and is utilized as an energy storage molecule within the microorganism's cellular structure. Due to its biodegradability and biocompatibility, this biopolyester may easily find industrial applications (Weber 2000; Lenz and Marchessault 2005). Potentially, polyhydrobutyrate offers many advantages over traditional petrochemically derived plastics in packaging applications, since it is compatible with many foods, such as dairy products, beverage, fresh meat products and ready meals. In addition to its complete biodegradability, it possesses better physical properties than polypropylene for food packaging applications and is completely non-toxic. However, as polyhydrobutyrate is a partially crystalline polymer with a high melting temperature and a high degree of crystallinity, then it is brittle and has limited applications (Hankermeyer and Tjeerdema 1999). The poor low-impact strength of polyhydrobutyrate is solved by incorporation of hydroxyvalerate monomers into the polymer to produce polyhydroxybutyrate-co-valerate (Liu et al. 2002). Polyhydroxybutyrate-co-valerate completely degrades into carbon dioxide and water under aerobic conditions (Lenz and Marchessault 2005).

Many papers report the use of polyhydrobutyrate for the preparation of polymer/clay nanocomposite materials (Park et al. 2001; Liu et al. 2002; Maiti et al. 2003; Chen et al. 2004). Instead, the formation of nanocomposite materials from polyhydrobutyrate seems to be difficult, and rather moderate improvements in properties have been reported in the case of polyhydrobutyrate as matrix material (Maiti et al. 2003). These results still have low mechanical properties with a low extension at break, which limits its range of applications. If the properties of the polyhydrobutyrate can be further improved by the addition of a small quantity of an environmentally benign material, this polymer will find numerous applications in packaging.

6.2.4 *Polycaprolactone*

Polycaprolactone is linear polyester prepared by either ring opening polymerization of 3-caprolactone using a variety of anionic, cationic and co-ordination catalysts or via free radical ring-opening polymerization of 2-methylene-1-3-dioxepane (Pitt 1990). It is a semicrystalline polymer with a high degree of crystallinity (around 50 %). Polycaprolactone exhibits high elongation at break and low modulus. Its physical properties and commercial availability make it very attractive as a material for packaging applications. Polycaprolactone is also interesting for applications in the biomedical (Chandra and Rustgi 1998; Okada 2002; Nair and Laurencin 2007) and agricultural areas (Nakayama et al. 1997).

Because of its low melting point, in conventional applications it must be blended with other polymers (Ishiaku et al. 2002; Lee et al. 2002; Lim et al. 2002). The blended of polycaprolactone with the fillers nanocomposites have been reported literature. The nanocomposites based on polycaprolactone/organically modified layered silicate with better physical properties have been developed (Bharadwaj et al. 2002; Di et al. 2003; Gorrasi et al. 2002, 2004; Tortora et al. 2002).

6.3 Improved Packaging

In improved packaging development, nanomaterials are mixed into the polymer matrix to improve the gas barrier properties, as well as temperature and humidity resistance of the packaging. A variety of nanoparticle reinforced polymers, also termed as nanocomposites have been developed, which typically contain up to 5 % w/w nanoparticles with clay nanoparticle composites with improved barrier properties (80–90 % reduction) for the manufacture of bottles for beer, edible oils and carbonated drinks and films (Chaudhry et al. 2008; Brody 2007). United States Food and Drug Administration (USFDA) have approved the use of nanocomposite in contact with foods (Sozer and Kokini 2009).

6.3.1 Nanocoatings

Coating in food can be defined as thin/film of edible material placed between food components to provide a barrier to mass transfer (Guilbert et al. 1997). These coatings could serve as moisture, lipid, and gas barriers. Coatings are applied and formed directly on the food product either by addition of a liquid film forming solution or by molten compounds (Baldwin et al. 1996). Components of edible coatings can be divided into two categories: water-soluble polysaccharides (hydrocolloids) and lipids. Suitable polysaccharides include cellulose derivatives, alginates, pectins, starches, chitosan and other polysaccharides (El Ghaouth et al. 1991). Many lipid compounds such as animal and vegetable fats have been used to make edible films and coatings. Suitable lipids include waxes, acylglycerols, and fatty acids. Lipid films have excellent moisture barrier properties or as coating agents for adding gloss to confectionery products. Waxes are commonly used for coating fruits and vegetables to retard respiration and lessen moisture loss (Avena-Bustillos et al. 1997).

Edible coatings are currently extensively used on a wide variety of foods, including fruits, vegetables, meats, chocolate, cheese, candies, bakery products, and French fries (Morillon et al. 2002; Cagri et al. 2004; Rhim 2004). However, until now only few research works reported the incorporation nano-particles toward coating films, in order to improve their physical properties. In order to lower the diffusion of oxygen, clay montmorillonite has been added into pectins (Mangiacapra et al. 2005). Similarly, a nanocomposites prepared by gelatin and montmorillonite has been used for considerable improvement of the physical properties (Zheng et al. 2002). An appreciable increase in stability of chitosan/layered nanocomposites was also developed (Darder et al. 2003).

Despite the lack of specific literature data, there is sufficient evidence to establish the beneficial effects of inorganic nanofiller on these materials, among which there are improved retention of flavor, sugars, acids, texture and color, increased stability during shipping and storage, improved appearance and reduced spoilage. Nanoparticles can be used as carrier of antimicrobials and additive. It can also be used to stabilize the additives and efficiently control their diffusion into the food and in the different regions, i.e., surface vs. bulk of a food system. This control can be interesting for long-term storage of foods or for imparting specific desirable characteristics, such as flavor to a food system. In this regards, an edible antibacterial nanocoating, which can be applied directly to bakery goods has also been developed by the U.S. Company Sono-Tec Corporation (El Amin 2007).

6.3.2 *Nanolaminates*

Nanotechnology provides food scientists with a number of ways to create novel nanolaminate films that suitable to be used in the food industry. Generallay, a nanolaminate consists of two or more layers of materials with nanometer dimensions that are physically or chemically bonded to each other. One of the most powerful methods in nanolaminated, is based on the layer by layer deposition technique, in which the charged surfaces are coated with interfacial films consisting of multiple nanolayers of different materials (Decher and Schlenoff 2003). Nanolaminates offer some advantages for the preparation of edible coatings and films over conventional technologies and may thus have a number of important applications within the food and dairy industry (Weiss et al. 2006).

A variety of different adsorbing substances could be used to create the different layers, including natural polyelectrolytes (proteins, polysaccharides), charged lipids (phospholipids, surfactants), and colloidal particles (micelles, vesicles, droplets) (Dasgupta et al. 2016a). It would be possible to incorporate active functional agents such as antimicrobials, anti browning agents, antioxidants, enzymes, flavors, and colors into the films. These functional agents would increase the shelf life and quality of coated foods. The basic functional properties of laminated films depend on the characteristics of the film-forming materials used for their preparation. Like nanocoating, these nanolaminated coatings could be created entirely from edible materials ingredients (proteins, polysaccharides, lipids) by using simple processing operations such as dipping and washing. The composition, thickness, structure, and properties of the multilayered laminate formed around the object could be controlled in a number of ways, including changing of the type of adsorbing substances in the dipping solutions, the total number of dipping steps used, the order that the object is introduced into the various dipping solutions, the solution and environmental conditions used, such as pH, ionic strength, dielectric constant, temperature, etc (Dasgupta et al. 2016b, c; Ranjan et al. 2015, 2016; Maddineni et al. 2015).

6.3.3 *Clay Nanoparticles and Nanocristals*

Nanoclays can be used to improved barrier properties of the food packaging materials by incorporating and embedding inside them. The layered silicates commonly used in nanocomposites consist of two-dimensional layers, which are 1 nm thick and several microns long depending on the particular silicate. Its presence in polymer formulations increases the tortuosity of the diffusive path for a penetrated molecule (Fig. 6.5), which in turn, providing excellent barrier properties (Bharadwaj et al. 2002; Cabedo et al. 2004; Mirzadeh and Kokabi 2007). The interaction between layered silicates and polymer chains may produce two types of ideal nanoscale composites as shown in Fig. 6.3. The intercalated nanocomposites result from the penetration of polymers chains into the interlayer region of the clay,

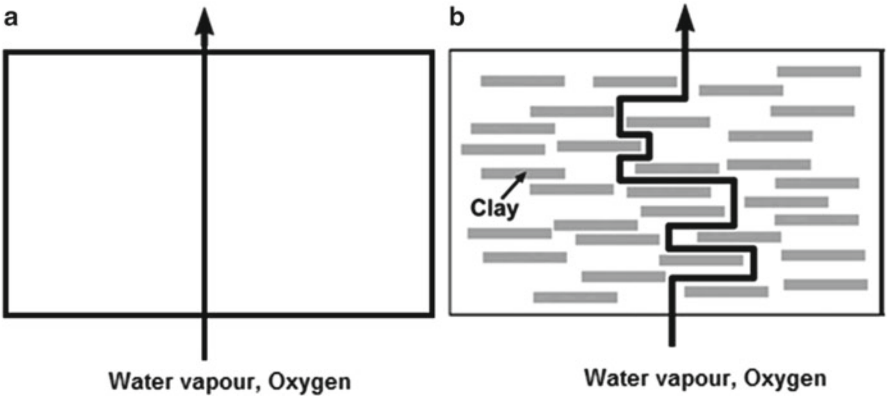

Fig. 6.5 Illustration of the "tortuous pathway" created by incorporation of exfoliated clay nanoplatelets into a polymer matrix film. In a film composed only of polymer (**a**), diffusing gas molecules on average migrate via a pathway that is perpendicular to the film orientation. In a nanocomposite (**b**), diffusing molecules must navigate around impenetrable particles/platelets and through interfacial zones which have different permeability characteristics than those of the virgin polymer. The tortuous pathway increases the mean gas diffusion length and, thus, the shelf-life of spoilable foods (Adapted from Adame and Beall 2009)

resulting in an ordered multilayer structure, with alternating polymer/inorganic layers at a repeated distance of a few nanometers (Weiss et al. 2006). The exfoliated nanocomposites involve extensive polymer penetration, with the clay layers delaminated and randomly dispersed in the polymer matrix (Luduena et al. 2007). Exfoliated nanocomposites were the best properties due to the optimal interaction between clay and polymer (Adame and Beall 2009; Alexandre et al. 2009).

The most widely studied type of clay fillers is montmorillonite, an hydrated alumina-silicate layered clay consisting of an edge-shared octahedral sheet of aluminum hydroxide between two silica tetrahedral layers (Weiss et al. 2006). The imbalance of the surface negative charges is compensated by exchangeable cations (typically Na^+ and Ca^{2+}). The parallel layers are linked together by weak electrostatic forces (Tan et al. 2008). This type of clay is characterized by a moderate negative surface charge, which is an important factor to define the equilibrium layer spacing. The charge of the layer is not locally constant as it varies from layer to layer and must rather be considered as an average value over the whole crystal (Alexandre and Dubois 2000). Montmorillonite is an effective reinforcement filler, due to its high surface area and large aspect ratio (50–1000) (Uyama et al. 2003).

Mostly nanoclays have been reported to improve the mechanical strength of several polymers (Avella et al. 2005; Chen and Evans 2005; Jawahar and Balasubramanian 2006; Mangiacapra et al. 2006; Russo et al. 2007; Cyras et al. 2008; Yu et al. 2003) and also of biopolymers, making their use feasible as packaging materials (Dean et al. 2007; Marras et al. 2008: Park et al. 2003; Petersson and Oksman 2006; Weiss et al. 2006; Xu et al. 2006). Other benefits have been reported on the performance of a diversity of polymers as resulting from using clay nanoparticles, including increased glass transition (Cabedo et al. 2004; Petersson and Oksman 2006; Yu et al. 2003) and thermal degradation temperatures (Bertini et al. 2006; Cabedo et al. 2004; Cyras et al. 2008; Paul et al. 2003; Yu et al. 2003). Furthermore, the advantage of clay nanocomposite in the packaging material offers improved shelf life, shutter proof, light in weight and heat resistant (Ravichandran 2010).

The minor disadvantages of nanoclays on polymers were decreased transparency (Yu et al. 2003). Some companies in the USA (e.g. Nanocor Inc. and Southern Clay Products, Inc.) was making plastics lighter, stronger, more heat-resistant and with improved barrier against gases, moisture and volatiles by incorporating montmorillonite in nanocomposite production (Moraru et al. 2003). Some industries have incorporated clays in nylon- 6, which is fluid and easily penetrates small spaces between layers. Nylon-6 nanocomposites can achieve oxygen transmission rates almost four times lower than that of neat nylon-6 (Brody 2003). Nanocor and Mitsubishi Gas Chemical (New York) have developed Imperm, a nanocomposite nylon MXD6 with much improved barrier properties, to be used in films and polyethylene terephthalate bottles (Brody 2006, 2007). The nanocomposite material can be used as an oxygen barrier layer in the extrusion manufacturing of bottles for fruit juices, dairy foods, beer and carbonated drinks, or as nanocomposite layers in multilayer films to enhance the shelf life of a variety of foods such as processed meats, cheese, confectionery, cereals, and boil-in-bag foods (Brody 2007; Moraru et al. 2003).

6.4 Active Packaging

In active packaging development, nanomaterials are used to interact directly with the food or the environment to allow better protection of the product. For example, silver nanoparticles and silver coatings can provide anti-microbial properties, with other materials being used as oxygen or UV scavengers. Nano silver, Nano magnesium oxide, nanocopper oxide, nano titanium dioxide and carbon nanotubes are also predicted for future use in antimicrobial food packaging (Chaudhry et al. 2008; Doyle 2006, Miller and Senjen 2008). Antimicrobial packaging for food products which absorbs oxygen has been developed and commercialized by Kodak company (Asadi and Mousavi 2006). Oxygen scavenging packaging using enzymes between polyethylene films have also been developed (Lopez-Rubio et al. 2006). An active packaging application could also be designed to stop microbial growth once the package is opened by the consumer and rewrapped with an active-film portion of the package (Brody 2007).

6.4.1 Antimicrobial Films

The incorporation of antimicrobial compounds (e.g. silver nanoparticles and silver coatings) into food packaging materials has received considerable attention currently. The films with antimicrobial activity could help control the growth of pathogenic and spoilage microorganisms. An antimicrobial film is particularly desirable due to its acceptable structural integrity and barrier properties imparted by the nanomaterial, and the antimicrobial properties contributed by the antimicrobial agents impregnated within the film (Rhim and Ng 2007). Here, the film allows nanomaterials to be able to attach more copies of biological molecules, which confers greater efficiency (Luo and Stutzenberger 2008).

Nanomaterials have been studied for antimicrobial activity so that they can be used as growth inhibitors (Cioffi et al. 2005), killing agents (Huang et al. 2005; Kumar and Munstedt 2005; Lin et al. 2005; Qi et al. 2004; Stoimenov et al. 2002), or antibiotic carriers (Gu et al. 2003). The most common antimicrobial films for food packaging are based on silver nanoparticles, which are well known for its strong toxicity to a wide range of microorganisms, with high temperature stability and low volatility (Kumar and Munstedt 2005). Film based on silver nanoparticles has been produced and their antimicrobial affectivity has been reported.

Nanocomposites with low silver nanoparticles content presented a better increased efficacy against *E. coli* than microcomposites with much higher silver in polyamide 6/silver-nano- and microcomposites (Damm et al. 2007, 2008). Moreover, silver nanoparticles absorbs and decomposes ethylene (Hu and Fu 2003), which may contribute to its effects on extending shelf life of fruits and vegetables. Indeed, nanocomposite polyethylene film with silver nanoparticles retarded the senescence of jujube, a Chinese fruit (Li et al. 2009). A coating containing silver nanoparticles was effective in decreasing microbial growth and increasing shelf life of asparagus (An et al. 2008). Silver nanoparticles increased modulus and strength of a poly(vinyl alcohol) matrix, and improved its thermal properties, enhancing its stability and increasing its Tg (Mbhele et al. 2003). Nanostructured calcium silicate has also been used that adsorb Ag^+ from solution down to the 1 mg/kg level (Johnston et al. 2008) as antimrobial film.

Other materials that have been used as antimicrobial materials are titanium dioxide (TiO_2), carbon nanotubes, nisin and chitosan. TiO_2 is widely used as a photocatalytic disinfecting material for surface coatings (Fujishima et al. 2000). TiO_2 photocatalysis, which promotes peroxidation of the polyunsaturated phospholipids of microbial cell membranes (Maness et al. 1999), has been used to inactivate several food-related pathogenic bacteria (Kim et al. 2003, 2005; Robertson et al. 2005). A TiO_2 powder-coated packaging film has been verified its ability to reduce E. coli contamination on food surfaces, suggesting that the film could be used for fresh cut produce (Chawengkijwanich and Hayata 2008).

Carbon nanotubes have also been reported to have antibacterial properties. Direct contact with aggregates of carbon nanotubes was demonstrated to be fatal for *E. coli*, possibly because the long and thin carbon nanotubes puncture microbial cells, causing irreversible damages (Kang et al. 2007). On the other hand, there are studies suggesting that carbon nanotubes are cytotoxic to human cells, at least when in contact to skin (Monteiro-Riviere et al. 2005) and lungs (Warheit et al. 2004), which would affect people working directly with carbon nanotubes in processing stages rather than consumers. Nevertheless, it is mandatory to know eventual health effects of carbon nanotubes when ingested, since the risk of ingestion of particles incorporated to a food packaging material must be taken into account because of the possibility of migration to food.

Antimicrobial peptides, such as nisin, could also be integrated with layer by layer structures to develop antimicrobial films (Haynie et al. 2006). Nisin acts as a depolarization agent on bacterial membranes and creates pores in lipid bilayers (Sahl et al. 1987). Multilayer peptide nanofilms, which intercalated different peptides designed to be oppositely charged at neutral pH which was much more stable than when the peptide film was stabilized only by electrostatic interactions (Li et al. 2006).

Antibacterial activity of nanoscale chitosan has also been reported (Qi et al. 2004). One possible antimicrobial mechanism involves interactions between positively charged chitosan and negatively charged cell membranes, increasing membrane permeability and eventually causing rupture and leakage of intracellular material. This is consistent with the observation that both raw chitosan and engineered nanoparticles are ineffective at pH values above 6, which would be due to the absence of protonated amino groups (Qi et al. 2004).

6.4.2 Oxygen Scavenging Film

Oxygen (O_2) is responsible for the deterioration of many foods either directly or indirectly. For example, direct oxidation reactions result in browning of fruits and rancidity of vegetable oils. Food deterioration by indirect action of O_2 includes food spoilage by aerobic microorganisms. Therefore, the incorporation of O_2 scavengers into food package can maintain very low O_2 levels, which is useful for several applications, since it will enhance self-life of the food.

Oxygen scavenger films were successfully developed by adding titania nanoparticles (TiO_2) to different polymers (Xiao-e et al. 2004). So that they can be used for packaging a wide variety of oxygen-sensitive products. Attention has particularly focused on the photocatalytic activity of nanocrystalline titania under ultraviolet radiation. Since TiO_2 act by a photocatalytic mechanism, and its major drawback is the requirement of UVA light (Mills et al. 2006).

6.4.3 UV Absorbing Films

Commonly used material as UV absorbing is film based on nanocrystalline titania (TiO_2). The efficacy of TiO_2-coated films exposed to sunlight to inactivate fecal coli forms in water has been demonstrated (Gelover et al. 2006). Metal doping improves visible light absorbance of TiO_2 and increases its photo catalytic activity under UV irradiation (Anpo et al. 2001). It has been reported that doping TiO_2 with silver greatly improved photo catalytic bacterial inactivation (Page et al. 2007; Reddy et al. 2007). This combination was resulted good antibacterial properties of TiO_2/Ag+ nanoparticles in a nanocomposite with PVC (Cheng et al. 2006).

6.5 Smart Packaging

In smart/intelligent, nanomaterials are used for sensing biochemical or microbial changes in the food, for example detecting specific pathogens developing in the food, or specific gases from food spoiling (Kuswandi et al. 2011). In terms of smart packaging, nanoparticles can be applied as reactive particles in packaging materials to inform about the state of the packaged product. The so-called nanosensors are able to respond to external stimuli change in order to communicate, inform and identify the product with the aim to assure its quality and safety. The recent developments for polymer nanomaterials for smart food packaging include spoilage indicators, oxygen indicators, product identification and traceability.

6.5.1 Nanosensors

Packaging equipped with nanosensors is also designed to track either the internal or external conditions of food products, pellets and containers, throughout the supply chain. For example, such packaging can monitor temperature or humidity over time and then provide relevant information of these conditions, for example by changing color. Nanosensors in plastic packaging can detect gases given off by food when it spoils and the packaging itself changes color to alert you. The so-called nanosensors are able to respond to environmental changes (e.g., temperature or humidity in storage rooms, levels of oxygen exposure), degradation products or microbial contamination (Bouwmeester et al. 2009).

Usually, producers estimated the expiration date of food by considering distribution and storage conditions, especially temperature to which the food product is predicted to be exposed. However, such conditions are not always known, and foods are frequently exposed to temperature abuse; this is particularly worrying for products which require a cold chain. Furthermore, sealing defects in packaging systems can lead food products to an unexpected high exposure to oxygen, which can result in undesirable changes. Nanosensors, when integrated into food packaging, can detect certain chemical compounds, pathogens, and toxins in food, being then useful to eliminate the need for inaccurate expiration dates, providing real-time status of food freshness (Liao et al. 2005).

They have also been reported that nano-biosensors already have been developed and commercialized to detect pathogens, spoilage, chemical contaminants, or product tampering, or to track ingredients or products through the processing chain (Nachay 2007). Nanosensors based on carbon nanotubes have also been pointed out to have several advantages over conventional detection methods such as high performance liquid chromatography. Carbon nanotubes based nanosensor is rapid and high-throughput detection; simplicity and cost effectiveness; reduced power requirements and easier recycling; and the un-necessity of exogenous molecules or labels. Furthermore, a multiwalled carbon nanotubes based biosensor have also been developed that can detect microorganisms, toxic proteins, and degraded products in food and beverages (Nachay 2007).

Engineered nanosensors have also been developed in packages to change color to warn the consumer if a food is beginning to spoil, or has been contaminated by pathogens using electronic "noses" and "tongues" to "taste" or "smell" scents and flavors (Joseph and Morrison 2006, Asadi and Mousavi 2006; Scrinis and Lyons 2007; Sozer and Kokini 2009). In real market applications, Nestlé, British Airways, MonoPrix Supermarkets are using chemical nanosensors that can detect color change (Pehanich 2006).

6.5.2 Freshness and Spoilage Indicators

Based on applied studies of the surface properties of materials, several types of gas sensors have been developed, which translates chemical interactions between particles on the surfaces into a response signal. Conducting polymers or electro active conjugated polymers, which can be synthesized either by chemical or electrochemical oxidation, are very important because of their electrical, electronic, magnetic and optical properties, which are related to their conjugated p electron backbones (Ahuja et al. 2007; Kuswandi et al. 2012). Polyene and polyaromatic conducting polymers such as polyaniline, polyacetylene, polypyrrole have been widely studied (Ahuja et al. 2007; Kuswandi et al. 2012). Electrochemically polymerized conducting polymers have a remarkable ability to switch between conducting oxidized (doped) and insulating reduced (undoped) state, which is the basis of many applications (Rajesh and Kaneto 2004). On-package indicator contains polyaniline film, that responds through visible color change to a variety of basic volatile amines released during fish spoilage period has been developed (Fig. 6.6) (Kuswandi et al. 2012). Color changes, in terms of total color difference of polyaniline, correlated well with total volatile amine levels and microbial growth patterns in fish samples (milkfish). These responses enabled the real-time monitoring of fish spoilage either at various constant temperatures or with temperature fluctuations.

Food spoilage is caused by microorganisms, whose metabolism produces gases which can be detected by conducting polymer nanocomposites or metal oxides, which can be used for quantification and/or identification of microorganisms based on their gas emissions as well as for food freshness detection. Sensors based on conducting polymer nanocomposites consist on conducting particles embedded into an insulating polymer matrix. The resistance changes of the sensors produce a

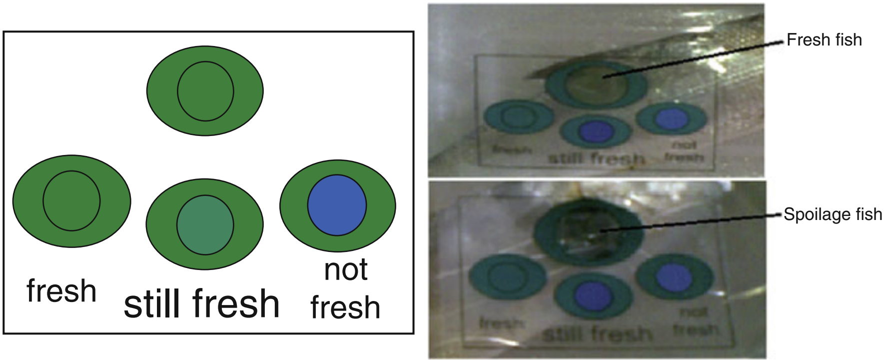

Fig. 6.6 Freshness sensor for smart packaging based on nanofibre of polyaniline. Left is sensor reference color change for detection of fish freshness, and right is sensor response towards fresh fish and spoilage fish (Courtesy of Kuswandi et al. 2012)

pattern that corresponds to the gas under investigation (Arshak et al. 2007; Kuswandi et al. 2012). Conducting polymer nanocomposites sensors containing carbon black and polyaniline have been developed to detect and identify food borne pathogens by producing a specific response pattern for each microorganism. Three bacteria, such as Bacillus cereus, Vibrio parahemolyticus and Salmmonella spp. could be identified from the response pattern produced by the sensors (Arshak et al. 2007). Chicken meat freshness was evaluated based on the smell when the output data of metal, such as tin and indium oxide gas sensors were processed with a neural network (Galdikas et al. 2000). An "electronic tongue" incorporated in food packaging have also been developed (Joseph and Morrison 2006). The device consists of an array of nanosensors extremely sensitive to gases released by spoiling microorganisms, producing a color change which indicates whether the food is deteriorated.

6.5.3 O_2 Indicators

Oxygen allows aerobic microorganism to grow during food storage. There has been an increasing interest to develop non-toxic and irreversible oxygen sensors to assure oxygen absence in oxygen free food packaging systems, such as packaging under vacuum or nitrogen. An UV-activated colorimetric oxygen indicator using UVA light has been developed, which uses nanoparticles of titania (TiO_2) to photosensitize the reduction of methylene blue by triethanolamine in a polymer encapsulation medium (Lee et al. 2005). Upon UV irradiation, the sensor bleaches and remains colorless, until it is exposed by oxygen, when its original blue color is restored. The rate of color recovery is proportional to the level of oxygen exposure. Nanocomposite thin films deposited methylene blue/TiO_2 on glass by liquid phase deposition, a soft chemical technique which has been applied to deposition of oxides to several substrates have been developed for oxygen indicator packaging systems in a variety of oxygen-sensitive foods (Gutierrez-Tauste et al. 2007).

Nanocrystalline SnO_2 has been used as a photo sensitizer in a colorimetric O_2 indicator comprising a sacrificial electron donor (glycerol), a redox dye (methylene blue), and an encapsulating polymer (hydroxyethyl cellulose) (Mills and Hazafy 2009). Exposure to UVB light led to activation (photo bleaching) of the indicator and photo reduction of methylene blue by the SnO_2 nanoparticles. The color of the films varied according to O_2 exposure – bleached when not exposed, and blue upon exposed.

6.5.4 Product Identification and Anti-counterfeiting

Some smart packaging has also been developed to be used as a tracking device for food safety or to avoid counterfeit. BioMerieux have developed a multi-detection test – Food Expert ID® for nano surveillance response to food scares. The nanotech company pSiNutria are also developing nano-based tracking technologies, including an ingestible BioSilicon which could be placed in foods for monitoring purposes and pathogen detection, but could also be eaten by consumers (Scrinis and Lyons 2007; Miller and Sejnon 2008). A United States company Oxonica Inc, has been developed nano-barcodes to be used for individual items or pellets, which must be read with a modified microscope for anti-counterfeiting purposes (Roberts 2007). Commercially available Nanobarcodes® manufactured by electroplating inert metals-such as gold, nickel, platinum, or silver- into templates that define the particle diameter, and then releasing the resulting striped nanorods from the templates (www.nanoplextech.com).

6.5.5 Active Tags and Traceability

Generally, active tags in packaging are radiofrequency identification. The tags are electronic information-based systems that uses radio frequency to transfer data from a tag attached to an object to trace and identify the object automatically. Radiofrequency identification is an improvement to the previous manual tracking systems or barcodes. Furthermore, it has a longer reading range, it is very strong and can work under extreme temperatures and different pressures, it can be detected at distances of more than 100 m, and many tags can be read simultaneously (Abad et al. 2007, 2009). Nanotechnology is also enabling sensor packaging to incorporate cheap radio frequency identification tags. The nano-enabled radiofrequency identification tags are much smaller, flexible and can be printed on thin labels. This increases the tags versatility and thus enables much cheaper production (www.thefreelibrary.com/).

6.6 Safety Issues

In terms of consumer safety, it is important to evaluate the potential migration of packaging constituents into food and to assess their potential hazard for a comprehensive risk assessment. However, to date very few studies have been published regarding the effects of nanomaterials upon ingestion, or the potential interaction of nanomaterial-based food contact materials with food components (Silvestre et al. 2011; Jain et al. 2016). In Europe, the legislation currently applies an overall migration limit of 10 mg constituent per dm^2 surface area to all substances that can migrate from food contact materials to foodstuffs (Commission Regulation (EU) No. 10/2011). For a liter cubic packaging containing 1 kg of food, this equates to a migration of 60 mg of substance per kg of food. However, with the exception of a few materials specifically listed in Annex 1 of the legislation, nanomaterial risk assessment has to be performed on a case-by-case basis (Silvestre et al. 2011; Commission Regulation (EU) No. 10/2011).

The migration of silver from three different types of nanocomposites into food stimulants, including an analysis of the form of silver migrating (ions or particles) has been studied (Echegoyen and Nerín 2013). Their results showed that silver migrated into food stimulants and that acidic food presented the highest level of migration. Moreover, heating was observed to increase migration, with microwave heating inducing more migration than a classical oven. The authors suggest that migration of silver could occur through two different mechanisms: the detachment of silver nanoparticles from the composites, or the oxidative dissolution of silver ions.

The migration of silver and copper from nanocomposites, used for their antimicrobial properties in food packaging has also been studied (Cushen et al. 2014). The study showed that the percentage of nanofiller in the nanocomposites was one of the most critical parameters driving migration, more so than particle size, temperature or contact time. A model to study migration of particles from food packaging has also been developed in this study. This model was a good predictor of the level of migration of nanosilver and to a lesser extent of nanocopper into food stuff and, when further developed and validated, could potentially be of benefit to industry by reducing the time and costs usually associated with migration studies.

More recently, the migration and toxicological profile of an organo-modified clay polylactic acid nanocomposite to be used as a food contact materials was evaluated. Migration studies indicated that less than 10 mg per dm^2 of the nanocomposite migrated in water, under the conditions of the experiment (Maisanaba et al. 2014a). Further analysis of the food stimulant indicated that the levels of metals measured were below the permitted values. In addition, the authors evaluated the potential toxicity of migration extracts both in vitro and in vivo. Assessment of the potential cytotoxicity of the migration extracts in vitro, on two cell types representative of the digestive system and their ability to induce DNA mutations, did not reveal any evidence of in vitro toxicity compared to control (Maisanaba et al. 2014a). Furthermore, exposure of rats to the same migration extracts for 90 days in drinking water did

Fig. 6.7 Relevant regulation for nano-packaging, including food product legislation and product safety directive, chemical safety regulation, and environmental regulation

not show evidence of toxicity in terms of oxidative stress, inflammation, clinical biomarkers and histopathological analysis (Maisanaba et al. 2014b).

These studies indicate the potential for nanomaterials to migrate from food contact materials into foodstuffs, with the rate of migration potentially associated with the percentage of nanofiller present in the composite material. There remains is a need for further migration and toxicological studies in order to ensure safe development of nanotechnologies in the food packaging industry. Thus, safe and successful implementation of nano-packaging applications need to fulfill three regulations, i.e. (i) food regulation, (ii) health regulation and (iii) environmental regulation as shown in Fig. 6.7. These are needed to ensure that society can benefit from novel applications of nano-packaging, whilst a high level of protection of health, safety and the environment is maintained. Furthermore, these are needed to ensure the safety use of these nano-packaging, with special emphasis in the enhancement of knowledge regarding their eventual toxicological effects, migration potential and levels of exposure for both workers and consumers, with special emphasis on the effects on the selected nanomaterials to human health following chronic exposure. In addition, it is necessary for the producers not only to assure product quality ensuring regulatory compliance but also to involve the consumer providing clear information in regard to benefits/possible risks balance and protection of the environment. If all regulation fulfils, then the fruitful of incorporation of nanomaterial into food packaging would play an important role in making the world's food supply healthier, safer, and tastier and more nutritious as well as environmental friendly.

6.7 Conclusion

Based on all the research conducted during last decade, clearly nanotechnology offers tremendous opportunities for innovative developments in food packaging that can benefit both consumers and industry. The application of nanotechnology shows considerable advantages in improving the properties of packaging materials, even in the early stages and will require continued investments to fund the research and development to better understand the advantages and disadvantages of nanotechnology use in packaging materials. The use of nanotechnology to fabricate food packaging can give numerous benefits in the range of advanced functional properties. They can bring to packaging materials with enhanced processing, health and packaging functionalities, shelf-life, transportability, and reduced costs.

Nanotechnology has the potential to improve foods, making them tastier, healthier, and more nutritious, to generate new food packaging functions, new food packaging, and storage. However, many of the applications are currently at an elementary stage, and most are aimed at high-value products, at least in the short term. In addition to this, nanomaterials can be used to make packaging that keeps the product inside fresher for longer extending the life of food and improving food safety. Smart packaging, incorporating nanosensors, could even provide consumers with information on the state of the food inside. Food packages are embedded with nanosensors that alert consumers when a product is no longer safe to eat. Sensors can warn before the food goes spoil or can inform consumers the exact nutritional status contained in the contents. In fact, nanotechnology will be change the fabrication of the entire packaging industry.

In spite of the great possibilities existing for food packaging based on nanomaterials, it is hoped that simple traditional packaging will be replaced with multifunctional smart packaging. The next generation of packaging materials will be able to fit the requirements of preserving perishable foods and other food products. By adding appropriate nanoparticles, it will be possible to produce packages with stronger mechanical, barrier and thermal performance. Nano-structured materials will prevent the invasion of bacteria and microorganisms as a concern for food safety. The nanosensors embedded in the packaging may alert the consumer if a food has deteriorated and cannot be consumed any more.

Regardless of how applications of nanotechnology in the food packaging sector are ultimately marketed, governed, or perceived by the public, it seems clear that the integrating of nanoscale material in packaging will continue to yield exciting and unforeseen packaging products. However, the potential dangers and ethical questions, that the use of this new technology should be responded wisely with more research and development regarding these issues. Therefore, successful and safe implementation of nanotechnology applications will require constant dialogue between the scientists and companies who invent them and the consumers who purchase them. If it succeeds, then the fruitful of incorporation of nanomaterial into food packaging may play an important role in making the world's food supply healthier, safer, tastier, more nutritious and plentiful as well as environmental friendly.

Regulatory bodies, should author guidance with respect to the criteria to be followed in evaluating the safety of food packaging, uses of nanomaterials with novel properties and functions. Novel methods, approaches and standardized test procedures to study the effects of nanomaterials upon ingestion, or the potential interaction of nanomaterial-based food contact materials with food components are urgently needed for the evaluation of potential hazards relating to human exposure to nanoparticles. Even though, it is widely expected that nanotechnology-derived food packaging will be available increasingly to consumers worldwide in the coming years.

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Chapter 7
Nanotechnology in Food Processing and Packaging

Preetam Sarkar, Syed Irshaan, S. Sivapratha, and Ruplal Choudhary

Abstract Food products are complex mixtures including proteins, carbohydrates and lipids that are shaped at the nanoscale. These food nanomaterials are either naturally present within foods or created during transformation of initial products. Recent research has revealed several applications of food-based nanomaterials for food processing and packaging. For instance nanoparticles protect and control the delivery of antimicrobial compounds, lipid-soluble vitamins, flavours and antioxidants. Nanoparticles are also used as delivery vehicles such as pickering emulsions, multi-layered emulsions and solid-lipid nanoparticles. Nanosensors can detect rapidly toxic substances in food. In food packaging, nanoparticles can protect functional ingredients such as antimicrobials or vitamins. Chitosan nanoparticles are used as antimicrobial compounds to enhance food safety.

Keywords Nanoparticles • Nanocomposites • Food packaging • Nanosensors • Product quality

7.1 Introduction

7.1.1 Food Systems and Structures

In the modern world with urbanized lifestyle, food habit of people has become responsible for many disorders which were not a big concern a few decades back. People have to be conscious of what food they consume and how much they consume. Hyperglycaemia and obesity are two such disorders that are strangling millions of people directly or indirectly. A necessity is felt to produce foods that are

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nutritionally superior; at the same time safe, affordable and tasty. Although nutritious food can be delivered at the expense of organoleptic quality, humans always give preference to the food that satisfies their tongue. When food technologists develop food that is nutritionally superior and that has satisfactory mouth feel, the cost of such preparations shoot up and hence, their availability is restricted only to a narrow category of people (Boland et al. 2014). The task of making available nutritious, tasty and affordable food is hindered by a lot of interlinked factors. The in-depth understanding of food systems and structures are necessary to overcome these hindrances.

In general, food from animal and plant origin in their pristine form, are observed to have a 'fibre matrix' composite structure. A fibre is described as the one whose length to width ratio is more than 100. It implies that fibres are arranged in a certain fashion, like parallel, spiral, which may vary from commodity to commodity. These fibres provide the mechanical strength to hold the matrix material. Both the fibre and matrix are composed of polysaccharide and protein polymers. Polysaccharide polymers are cellulose and hemicellulose while protein fibres include actin, myosin, to name a few. Combination of proteins and polysaccharides like glucose aminoglycans act as matrix material that bind to the fibre (Vincent 2008).

Most of the food commodity from natural origin undergo milling, polishing, refining and numerous other processes, all meant to disturb the native fibre matrix structure. Therefore, food in consumable form is a derivative of the natural raw materials whose structure is spoken in terms of emulsion, particle, gel, and foam; indicating that the perspective used to view food structure could be colloidal (Boland et al. 2014). Emulsions that use solid nanoparticles to stabilise their structure are referred to as Pickering emulsion (Chevalier and Bolzinger 2013). Studies also make use of nanoparticles to stabilise foams in the food area and such foams have better stability (Bournival and Ata 2015; Rodríguez et al. 2015). There are several attempts to produce food innovations using nanotechnology.

Currently, more interest is drawn in the application of nanotechnology to food and agricultural sector. With the emergence of concepts such as green nanotechnology, more engineered nanomaterials are expected to hit the market. But the scientific community is yet to understand the new properties of engineered nanoscale materials (Chen et al. 2014b). Majorly work was carried in the area of application of nanoscale science to various sectors such as food packaging for extension of shelf life, sensors for detection of harmful compounds and to ensure food safety.

With the progress of food nanotechnology various novel methods for smart delivery of multifunctional components to target sites are being investigated. Currently, research is heading at creation of food systems with optimized delivery system and acceptance (physical, visual and sensory appeal) for providing human health care (Ravichandran 2010).

Recently, there is an enormous increase in the number of patents, publications and intellectual property rights in the budding field of agri-food nanotechnology (Dasgupta et al. 2015). Fortified 'canola active oil' enriched with phytosterols is developed by Shemen Industries Ltd. (Haifa, Israel). Fat soluble nutrients are converted to water soluble nutrients and its absorption is increased by products developed by Nutri-Nano™, CoQ-10 Solgar (Leonia, NJ, USA) (Ranjan et al. 2014).

Various products in the market related to food nanotechnology are Slim Shake Chocolate (based on Nanoclusters™ system), in which silica nanoparticles are coated with cocoa for enhancement of chocolate flavour. Similarly, Nano cluster™ is another delivery system based product from RBC Life Sciences® Inc (Dasgupta et al. 2015). FDA has approved the carotenoids and lycopene of tomato (particle size of 100 nm, from BASF's US patent US5968251) produced synthetically and are GRAS (Ranjan et al. 2014). Nano-micelle based products with intended use in food applications are produced by Novasol® from Aquanova® AG (Darmstadt, Germany). They are used to encapsulate the functional ingredients such as beta-carotene, vitamin A and lutein (Ranjan et al. 2014).

7.1.2 Food Packaging

Packaged articles are everywhere and packaged food is no exception. Literally everything in the market comes suitably packed for easy transportation from the centralized manufacturing facility, convenient transportation, comfortable handling, attractive displaying, easy costing, controlled dispersing and disposing. Therefore, packaging is inevitable in food industry.

Packaging is a process in which food products are well contained and protected from outside contamination for the ultimate convenience of the consumer and also communicates about the contents it possesses within (Robertson 2012). Packaging should deliver the food to the customer in a form most suitable for its use (Lockhart 1997). Packaging could be primary- the package that acts as a barrier between the food and the immediate environment. A primary packaging material contacts the food directly. The packages over primary package meant for the convenience of handling and transportation are referred to as secondary and tertiary packaging. Unitisation of primary packages is achieved using secondary package. For example, extruded snack foods packed in multilayer pouches is considered a primary package and it put into corrugated paperboard cartons is secondary packaging. A stretch wrapping over the corrugated cartons would be tertiary packaging. Metal shipping containers and crates are referred to as tertiary packaging which may or may not be used (Robertson 2012).

Large scale production, distribution and the success of delivering the food product in the intended form to the customers have covered up the added cost of manufacturing the packaging material, filling and sealing. Packaging ensures safe delivery of billions of food packs all over the world thus reducing food wastage. Food wastage not only means loss of product due to spoilage but additional cost gets piled up due to disposal issues (Coles et al. 2003).

The drive for packaging development in earlier days was largely given by military requirements during the world wars I and II. Packaging innovations such as polyethylene, aluminium foil, polyvinylchloride, beer cans, aseptic packaging, flexographic printing and packaging machinery were brought to use to cater to the food requirement of military personnel performing at harsh climates (Brody et al. 2008).

The present day drive for accelerating packaging innovation is changing lifestyle where people prefer to spend less and less time on preparing food from fresh produce. As of now we require ready-to-eat foods, microwavable foods and snacks that taste good and are nutritious. Such food distribution systems are provided by a variety of corporations around the world and packaging material, their graphics and information serve as platforms to advertise their respective brands (Yam and Lee 2012).

The most common packaging material in use these days are paper based, polymer based, metal based or the combination (laminates and co-extrudates) of the aforesaid. A single polymer used alone may not sufficiently give the adequate barrier properties under all situations. Therefore, multilayer packaging materials came into play. New innovations happen to come with a new problem. Multi-layered packages have many additives and layers making recycling difficult over the widely known trouble of non-degradability of polymer packages (Duncan 2011).

Bio-based packaging material claim degradability. These include starch fillers or gelatinised starch incorporated up to 75 % to low density polyethylene along with pro-oxidative additives. The fact that they don't actually degrade but just fragment have left many consumers with a deceived feeling. It should be noted that paper is not included under bio-based packaging material as the raw material should be annually renewable. Paper wood takes about 25–65 years to develop adequately (Chiellini 2008). Endless are the beneficial uses of packaging, yet, they are considered as an unnecessary cost. Some customers view it as a nuisance to the environment. This is because by the time the package is received by the consumer most of its functions are already over (Robertson 2012).

7.1.3 Introduction to Nanotechnology

7.1.3.1 Basics of Nanomaterials

The manufacture of structures in the size range of 1–100 nm and their use in various applications is termed as nanotechnology (Coles and Frewer 2013). Nanotechnology is an association of various disciplines like physics, chemistry and engineering and involves manipulation of the matter at the nanoscale (Tarver 2006). A structure that has at least one dimension in the nanometre range is called a nanostructure. A number of nanostructures have been made which are quantum dots (Tsakalakos et al. 2012), wires, wells, carbon nanotubes, and spherical nanoparticles that have a wide range of applications. Natural food components like protein and carbohydrates from natural resources can form nanoparticles. Cellulose is a natural polymer carbohydrate. Cellulose nanocrystals are synthesised by acid hydrolysis of cellulose from natural sources like wood and cotton (Khan et al. 2012).

7.1.3.2 Properties of Nanomaterials

What makes nanomaterials so special? The answer is different optical, electrical, and magnetic properties. The large surface energy associated with a high surface area of nanoparticles is responsible for special properties. The large surface area to volume ratio becomes very significant at the lower scales of nanometers. If an iron cube was cut from 1 cm^3 into smaller cubes, until the cube dimension was 1 nm^3, the ratio of number of surface atoms to bulk atoms would change from 1:10^6 to 1:0. The latter implies that every atom of the 1nm^3 nanocube is a surface atom. As number of atoms on the surface increases and so does the surface area with respect to the volume of the nanoparticle (Cao 2004).

Depending on the nature of nanoparticle the measured properties are varied. Nanospheres and nanofibrils have been associated with different food applications and hence different properties. Also, peptide and polysaccharide nanomaterial properties have variation from the properties of metal and metal oxide nanoparticles. For instance, persistence length and contour length are the properties of nanofibrils (protein based). Contour length is the maximum length at completely extended form while persistence length is the length of the polymer bent by thermal fluctuations (MacKintosh 1998). The high aspect ratio of protein fibrils affects the rheological property of the food solution. Gelling and thickening is enabled at comparatively low concentration of protein nanofibrils (Loveday et al. 2011). Metal oxide, food grade TiO_2 was characterised with crystal structure, surface composition, size and elemental composition (Yang et al. 2014).

7.2 Nanoscience in Food Processing

Nanoscience is the study of behaviour and properties related to nanostructures (Hochella 2008). Structuring of food systems at nanoscale will modify their inherent characteristics which will, in turn, assist in modulation of food quality at macroscale. Along with formulation and preparation, processing is an important unit operation that influences the physicochemical properties of food. It has a significant effect on altering the structure of food which influences their characteristics such as texture, flavour release profile, stability and other physicochemical properties (Huang 2012). In order to optimize the characteristics of food systems at nanoscale, in-depth knowledge on relationship between structure and properties of food is a prerequisite (Aguilera and Lillford 2008). This chapter reviews the various effects of food processing on quality and safety of foods systems.

7.2.1 Role of Nanotechnology in Food Quality

The structure and quality of food systems is greatly altered during food processing and it relies upon the various unit operations or processing conditions (temperature, pressure and mechanical forces) they are subjected to. Processing mainly influences the internal components of food namely protein, starch, and lipids (Raynes et al. 2014). The stabilization of bioactive materials encapsulated in nano-carrier systems against deleterious environmental conditions can be achieved by food nanotechnology and thus increase the nutrition and quality of food systems.

Eugenol extract is found to possess antibacterial and antifungal properties. It also possesses antioxidant properties which makes it suitable for preservative action. But it is susceptible to adverse environmental conditions such as heat and light. Thus to uphold the preservative action research has been carried for the formation of thermally stable eugenol by its encapsulation in (α, β and γ) cyclodextrin inclusion complex (Gong et al. 2016).

7.2.1.1 Encapsulation and Delivery Systems

Improper diet selection and poor eating patterns have led to very less or limited consumption of bioactive nutrients. As a consequence, health related issues like cancer, and cardiovascular diseases are prevailing. Currently, more emphasis has been drawn on improved food processing techniques to deliver the bioactive nutrients to overcome these health problems (Lindsay and Saarela 2011).

Encapsulation is the science of entrapment of desired functional component in a shielding material by mechanical or physicochemical process which results in the production of encapsulates ranging in diameter of few nanometers to millimetres (Chen and Chen 2007). It is widely used in agro-food industries for improving the quality and safety of food systems and has various functions such as masking and controlled release of flavours, inhibition of oxidation for enabling prolonged shelf life, smart delivery of nutrients and protection of probiotic microorganisms (Burgain et al. 2011).

Nano structuring and encapsulation of food systems is done for improved stability, controlled release of bioactive components (lipids and nutrients) to targeted sites (Huang 2012). Bioactive ingredients are entrapped and shielded inside the secondary matrix which will be released upon stimulus by the outside chemical environment (Onwulata 2012). Currently, special focus has been drawn at designing of colloidal delivery systems for effective delivery of hydrophobic bioactives for their use in food applications (McClements 2015). The design of encapsulation systems for delivery of core active ingredients to liquid food systems is demanding research as these functional components are hardly soluble in liquid medium or prone to degradation due to incompatibility between functional component and surrounding matrix (Sagalowicz and Leser 2010). Various nano delivery systems are available for the smart delivery of bioactives. In the recent years, mainly emphasis has been given

Table 7.1 Nano particle based delivery systems for nutrient encapsulation

Sl no.	Bioactive nutrient	Delivery vehicle	Components forming delivery vehicle	Reference
1	Docosahexanoic acid (DHA)	Nano-micelles	Casein	Zimet et al. (2011)
2	Vitamin B_2 (riboflavin)	Nano-capsule	Alginate/chitosan	Azevedo et al. (2014)
3	β-carotene	Lipid nanoparticles	Cocoa butter and/or hydrogenated palm oil, surfactant -Tween 80	Qian et al. (2013)
4	Vitamin D	Nanoemulsion	Tween 20, 40, 60, 80 and 85 and medium chain triglycerides (MCT)	Guttoff et al. (2015)
5	Vitamin E	Nanoemulsion	MCT oil and surfactant mixture Tween 80/Brij 35	Laouini et al. (2012)
6	Vitamin E	Nanoemulsion	Whey protein isolate and gum arabic and edible mustard oil with Tween surfactant.	Dasgupta et al. (2016a) and Ozturk et al. (2015a)
7	Vitamin D_3	Nanoemulsions	Surfactant-quillajasaponin	Ozturk et al. (2015b)
8	Lycopene	Nanoemulsions	Tween 20	Ha et al. (2015)
9	Curcumin	Core–shell nanoparticles	Protein (zein) as the core and polysaccharide (pectin) as the shell	Hu et al. (2015)

on delivery systems such as liposomes, nanoliposomes, nanoemulsions, nanostructured lipid carriers, nanosuspensions, nanoparticles, micelles, Pickering emulsion, solid lipid nanoparticles and are discussed as follows (Table 7.1; Fig. 7.1):

1. Liposomes: A liquid core is enclosed in a phospholipid bilayer in a spherical shell-like structure and is called as liposomes (Singh et al. 2012) (Table 7.2).
2. Nanoliposomes: Liposomes having dimensions of less than 200 nm are termed as nanoliposomes (Livney 2015).
3. Nanoemulsions: The colloidal dispersion made by a combination of several minute liquid droplets leads to the formation of nanoemulsions, which have a diameter <100 nm. They are classified as oil-in-water or water-in-oil or combination of both (bi-continuous). Similarly, it can be liquid in solid, or liquid in liquid. Nanoemulsions are produced by homogenization method such as high shear homogenization (Walker et al. 2015).
4. Nanostructured lipid carriers: These are combinations of different types of lipids mixed together, aimed at reducing the degree of crystallinity to control the microstructure and release profile (Davis et al. 2015).
5. Nanosuspensions: The systems in which solid nanoparticles are distributed in a continuous liquid medium and are stabilized by amphiphiles are termed as nanosuspensions (Livney 2015).

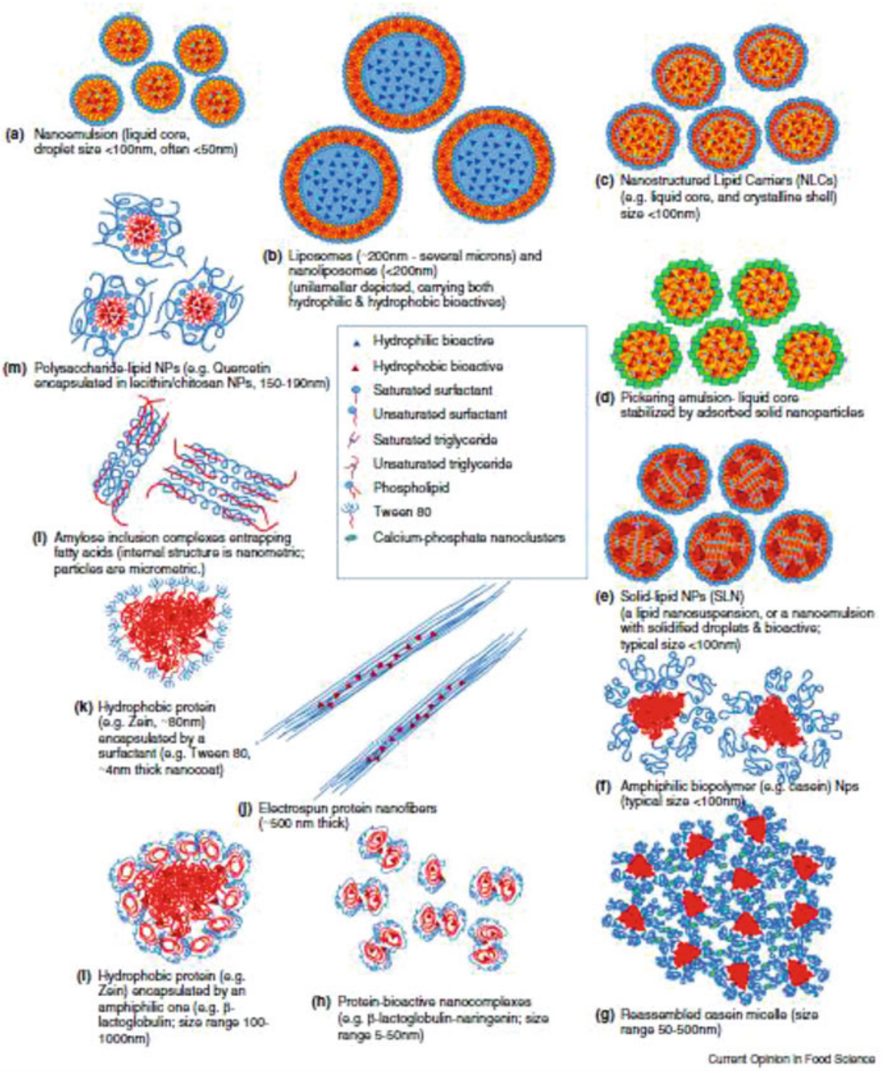

Fig. 7.1 An overview of different delivery vehicles in food nanotechnology

6. Pickering emulsion: Emulsions which are stabilized by particles are called as Pickering emulsions. The various particle stabilizers used for formation of Pickering emulsions are namely alumina, clay particles, chitin, silica, wax (Song et al. 2015).
7. Solid lipid nanoparticles: These are composed of lipids having melting point above room or body temperature (Davis et al. 2015).

Table 7.2 Delivery of antimicrobial compounds using nanostructured vehicles

Sl. no.	Antimicrobial component	Delivery vehicle	Components used to form delivery vehicle	Tested species	References
1	Nisin	Liposomes	Marine lecithin and soy lecithin	*Listeria monocytogenes*	Imran et al. (2015)
2	Nisin	Nanocapsule	Chitosan-carrageenan	*Micrococcus luteus*, *Pseudomonas aeruginosa*, *Salmonella enterica* and *Enterobacter aerogenes*	Chopra et al. (2014)
3	Pediocin	Nanocomposite film	Methyl cellulose film and ZnO nanoparticles	*Staphylococcus aureus* and *Listeria monocytogenes*	Espitia et al. (2013)
4	Pediocin	Nanovesicles	Soybean phosphatidylcholine (phospholipid)	*Listeria monocytogenes*, *Listeria innocua* and *Listeria ivanovii*	de Mello et al. (2013)
5	Thymol and eugenol	Co-encapsulated nanocapsule	Spray-dried zein–casein	*Escherichia coli* O157:H7 and *Listeria monocytogenes*,	Chen et al. (2015)
6	Thymol and thyme oil	Inclusion complexes	β-cyclodextrin	*Escherichia coli*	Tao et al. (2014)
7	Thymol	Nanospheres	Ethylcellulose/methylcellulose	*Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*	Wattanasatcha et al. (2012)
8	Eugenol	Nanoliposomes	–	*Staphylococcus aureus*, *Escherichia coli*, *Salmonella enterica* serovar Typhimurium, and *Listeria monocytogenes*	Peng et al. (2015)
9	Carvacrol	Nanoemulsion	Peanut oil (carrier) and fluid soy lecithinpolysorbate Tween 20 and monoolein	*Escherichia coli*	Donsì et al. (2014)
10	Carvacrol	Nanoemulsion	Medium chain triglyceride (MCT) oil and Tween 80	*Salmonella enterica* serovar *Enteritidis* and *Escherichia coli*	Landry et al. (2014)
11	Trans-cinnamaldehyde	Nanoemulsion	Sunflower oil and Tween 20 and glycerol monooleate,	*S. cerevisiae* and *L. delbrueckii*	Donsì et al. (2012)
12	Trans-cinnamaldehyde	Nanoemulsion	Cinnamon oil and Tween 20	*Salmonella* Typhimurium and *Staphylococcus aureus*	Jo et al. (2015)

Flavour Encapsulation

In recent times, one of the major challenges faced by food industries is to limit the loss of flavour, which is attributable to unstable processing conditions and occurrence of several undesirable reactions such as chemical degradation and oxidation. Significant efforts have been made to resolve this issue, among which major approaches are encapsulation of aroma compounds using formation of starch-aroma inclusion complex, usage of emulsion as a delivery vehicle (Kasemwong and Itthisoponkul 2013). Similarly, efforts to control Maillard reaction in different food products was carried out so as to produce desired flavour and colour and to reduce toxicity (Troise and Fogliano 2013).

It is well-known fact that loss of flavour compounds increases with higher processing temperatures. Ultimately, novel food processing techniques are emerging with time to resolve these issues. Significant research was carried out to entrap aroma compounds in starch matrix for shielding them during thermal processing. Native starch and aroma compounds such as menthol and menthone were able to form V amylose inclusion complexes and were found to be stable at higher processing temperatures, varied conditions of pH and had prolonged storage time at high water activities (Ades et al. 2012). The complexation was found to increase with the increase in amylose content, as amylose has the ability to form more molecular inclusion complexes among both glucose polymer units of starch, amylose and amylopectin. The helical structure of amylose has a hydrophobic cavity in which the volatiles (Kasemwong and Itthisoponkul 2013) and essential oils (Marques 2010) were entrapped.

The study to evaluate the flavour release profile with the presence and absence of α-amylase enzyme revealed that the amylose-flavour complex gets hydrolysed during chewing mechanism in the presence of enzymes and leads to complete release of aroma. It is also seen that the encapsulation efficiency between amylose-flavour complexes can modulate the release and retention of aroma compounds (Ades et al. 2012).

In another study, use of cyclodextrins for encapsulation of aroma compounds was emphasised. A general schematic of flavour encapsulation with cyclodextrins is demonstrated in Fig. 7.2. Commercially three types of cyclodextrins are available: α, β and γ cyclodextrins (Astray et al. 2009). Structurally, these are cyclic oligosaccharides produced as a result of starch degradation and own a truncated cone shape with hydrophobic cavity, whose diameter ranges from 5.7 to 9.5 A^o and hydrophilic exterior. This cavity enables flavour molecules to get trapped inside and form an inclusion complex with polyphenolic compounds (Pinho et al. 2014).

An experimental study was conducted to evaluate the retention of flavours (benzaldehyde, l-menthol, citral and vanillin) in various thermally processed food applications like candy, fruit leather and angel cakes. The flavours were made to form a molecular inclusion complex with β-cyclodextrins and they were compared with that of normal liquid formulations. As a consequence, it was found that flavour loss was minimised owing to increased heat stability due to complexation of flavours with β- cyclodextrins. The flavours benzaldehyde, citral and menthol had 20, 26 and

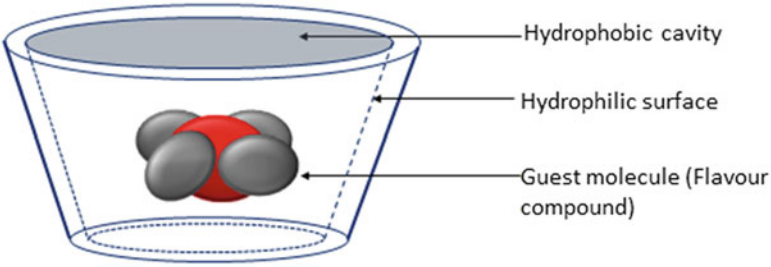

Fig. 7.2 Schematic representation of molecular inclusion complex between cyclodextrin and a flavour molecule

86-fold retention, respectively while complexing with β-cyclodextrins when compared with liquid formulations (Reineccius et al. 2004).

Thymol is a volatile phenolic compound, although it is found to be an antimicrobial in nature and effective against *Salmonella* Typhimurium, it has low acceptance owing to unpleasant bitter taste (Si et al. 2006). Another phenolic compound, resveratrol has a role in improving human health attributable to functional properties such as anti-carcinogenic, anti-inflammatory and protects heart functioning (Davidov-Pardo and McClements 2014). Research was performed to mask the undesirable taste of thymol by encapsulating it in cyclodextrins (Nieddu et al. 2014). Encapsulation technique is used to mask the unpleasant taste caused due to phenolic compounds and which influences the acceptance of a commodity. It even helps to enhance the stability and bioavailability of phenolic compounds (Fang and Bhandari 2010).

Electrospinning technique is used widely in recent times for formation of nano fibrous polymeric membranes (Mascheroni et al. 2013). Vanillin-cyclodextrins (α, β and γ) inclusion complex was formed in polyvinyl acetate nano-web by the use of electrospinning technique. The results suggested that vanillin and γ- cyclodextrins had slow and prolonged release of vanillin and was thermally stable when compared to other types of cyclodextrins (Kayaci and Uyar 2012).

In another study, carbohydrate polymers of pullulan and β-cyclodextrins were blended by electrospinning technique for production of encapsulates containing aroma compounds which are thermally stable and whose aroma release triggers on stimulus of humidity in surrounding environment (Mascheroni et al. 2013). Similarly, emulsion electrospinning process is used for encapsulation of limonene in polyvinyl acetate fibrous membranes (Camerlo et al. 2013).

Great attention has been paid to encapsulation of citral flavour attributable to its enormous application in beverages. Citral flavour is prone to degradation with time due to oxidation and results in loss of aroma intensity (Maswal and Dar 2014). The flavour release behaviour of six fragrances such as citronellal, camphor, eucalyptol, menthol, limonene and 4-tert-butylcyclohexyl acetate was evaluated after encapsulating them in various polymer based blends using solvent displacement technique.

The process resulted in good fragrance loading capacity and encapsulation efficiency of more than 40 % and 80 %, respectively. Limonene showed the fastest release while menthol had the slowest release profile (Sansukcharearnpon et al. 2010).

Some recent studies have been carried on aroma partition properties of oil–gel complexes. The gel structure made of monoglycerides forms a basis for encapsulation of oil. The gel was subjected to characterization and by application of headspace gas chromatography analysis the aroma partition properties were evaluated (Calligaris et al. 2010).

Nutrient Encapsulation

Carotenoids, mainly β carotene is the precursor of vitamin A and it plays a major role as an antioxidant (Böhm et al. 2002). It eradicates occurrence of health associated risks such as cancer, night blindness and cardiovascular diseases (Fikselova et al. 2008). These functional components are lost during processing since they are sensitive to heat and light (Rodriguez-Amaya 1999). Several methods have been deployed for increasing stability, smart delivery and bioavailability of β-carotene in food systems by nanoencapsulation. Novel carrier systems such as lipid nanoparticles, solid lipid nanoparticles and nanostructured lipid carriers are designed having improved functions such as increased bioavailability of active components, membrane permeability for controlled release (Gutiérrez et al. 2013).

Proteins and polysaccharides are used as carriers of active ingredients such as vitamins, ω-3 oils (Matalanis et al. 2011). Electrospray technique is used to produce microcapsules which assists to encapsulate proteins (Fukui et al. 2010). Carbohydrate particles are used for the encapsulation and improving bioavailability of catechins (Peres et al. 2011).

Microencapsulation technology has been a solution to solve the issues pertaining to stability of oils. The recommended daily intake for adults for both docosahexaenoic acid and eicosapentaenoic acid for maintaining cardiovascular health and coronary heart disease is 500 mg and 900 mg, respectively (Shi 2006).

Bioactive Lipids

Nanoliposomes are lipid vesicles which act as nanocarriers systems for the delivery of bioactive lipids. The lipid vesicles are composed of phospholipid molecules, main components in naturally occurring bilayers and show amphiphilic character (Siegel and Tenchov 2008). The presence of both lipid and aqueous phase makes it suitable for entrapment and controlled release of water and lipid soluble as well as amphiphilic materials (Mozafari and Mortazavi 2005). Liposomes are available in our natural diet, such as milk, eggs and can be easily approved for food use by regulatory bodies (Reza Mozafari et al. 2008).

In recent decades, the functional properties of lipids have been studied extensively. Functional lipids are encapsulated into nanoparticles for enhancing the bioavailability. Emulsification has been found to be one of the best technique for effective delivery of lipid molecules (Neves et al. 2015). Novel methods such as microchannel emulsification and nanochannel emulsification were proposed for production of droplets of very narrow size (Kobayashi et al. 2002).

Delivery of Probiotic Microorganisms

Probiotic encapsulation aims at protection and delivery of beneficial microorganisms from adverse environmental conditions. The study of yeast encapsulation reveals that the electrospray technique can encapsulate a physiologically active substrate in the polyelectrolyte microcapsule and maintain its activity (Fukui et al. 2010). Bioactive food components are classified into two types, molecules which are functional (bioactive molecules) and living cells which are beneficial (probiotics) (de Vos et al. 2010).

7.2.1.2 Sensory and Texture Improvement

Application of nanotechnology to food has led to improvement in sensory aspects such as taste, color, texture and modulation of consistency in food systems (Restuccia et al. 2010).

Color

Not much of research has been progressed in this field, recent research suggests the application of β-carotene, a fat soluble pigment to manipulate the colour of food systems by the application of nano-emulsion technology. The colour of food system varies from yellow to dark orange, and varies with the concentration of β-carotene in the nanoparticles (Cushen et al. 2012). Transparent and thermally stable dispersions which are of nano size are produced by encapsulation of eugenol using Maillard-type conjugates. Study was conducted for delivery of lipophilic components without affecting the visual characteristics (Shah et al. 2012).

Viscosity

Change in viscosity of food systems influences the flavour perception. With the increase in viscosity of foods there is a decrease in flavour release profile and thus leads to decrease in overall flavour intensity. It also delays the tastant signals of taste buds which lead to modulation of flavour perception (Taylor et al. 2009).

Size

Oil droplet size distribution is an important emulsion property which controls the release of aroma compounds. A study carried out to determine the effect of droplet size on aroma release profile has revealed that in the case of hydrophobic esters (e.g. geranyl acetate) with a decrease in droplet size of emulsion there was a significant increase in the release of aroma compounds while maintaining the oil content of emulsion. But the same trend was not found in case of ethyl butanoate which happens to be more hydrophilic ester (Weel et al. 2004).

7.2.2 Role of Nanoscience in Food Safety

Microbiological safety and security of food systems is a high priority issue in recent times as they are prone to contamination with pathogenic and spoilage microorganisms. Many costly and conventional methods, such as modification of atmosphere, high temperature and pressure are in use for ensuring food safety aspects. In the last decade, novel techniques are used in the delivery of entrapped active components such as nanoparticles, emulsion and hydrogels (Onwulata 2012).

7.2.2.1 Delivery and Protection Systems of Antimicrobial Agents

The Centre for Disease Control and Prevention has estimated in their findings that out of every six American people, one gets sick and hospitalized attributable to foodborne diseases. In terms of estimated number of illness, the main pathogens leading to hospitalizations and deaths each year are Norovirus, *Salmonella*, *Clostridium perfringens*, *Campylobacter spp.*, *Staphylococcus aureus*. Recently, with rapid consumer awareness on food safety and quality related issues there is demand for natural antimicrobials in food applications (Weiss et al. 2009). Thus, great attention is paid for protection of antimicrobial compounds present in natural sources to enhance food safety and security. Researchers have focused on design and development of novel delivery vehicles such as phytoglycogen based Pickering emulsions for the prolonged protection and release of bioactive agents such as nisin (Bi et al. 2011).

Antimicrobial silver nanoparticles with a size range of 20–30 nm were synthesized from dry roasted *Coffea arabica* seed extract by bio-reduction (Dhand et al. 2016). Silver nanoparticles with bactericidal potential were synthesized by chemical reduction method from the bark extracts of the plant species *Ficus benghalensis* and *Azadirachta indica*. An indication of formation of silver nanoparticles was the color change to dark brown, an observation further confirmed by ultraviolet-visible spectroscopy (Nayak et al. 2016). Cu-chitosan nanoparticles demonstrated antifungal activity, reduction of mycelial growth and inhibition of spore germination in tomatoes (Saharan et al. 2015).

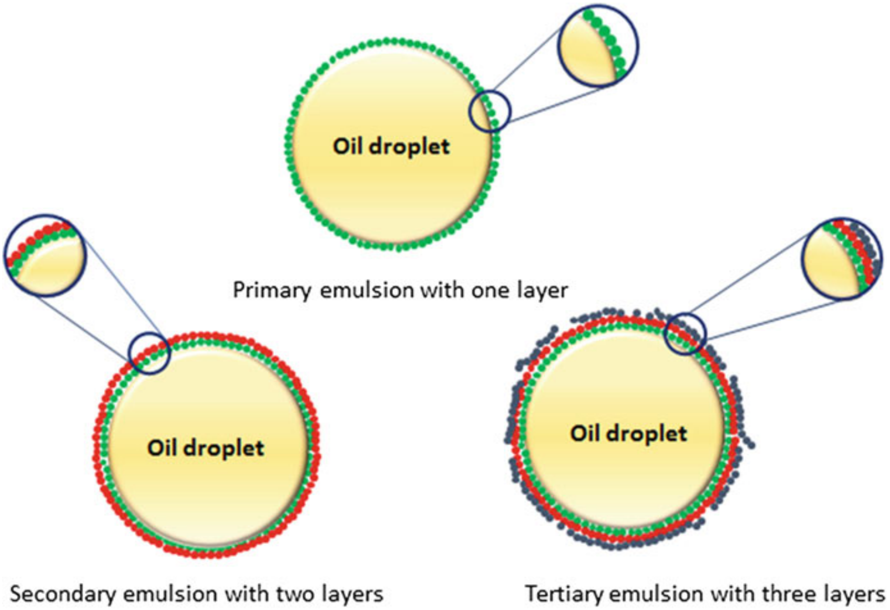

Fig. 7.3 Schematic representation of different types of oil-in-water emulsions with single and multiple interfacial layers

Emulsions

Various lipid-based vehicles have been proposed as delivery systems and for application in food system such as conventional emulsions, multiple emulsions, multilayered emulsions (McClements et al. 2009). These emulsion systems are used for prolonged delivery of antimicrobial compounds in food applications (Fig. 7.3).

Emulsion formulation and droplet size have been regarded as major parameters for evaluating the antimicrobial efficacy (Speranza et al. 2015). With the application of high pressure homogenization technique with an applied pressure of 300 MPa, nanoscale emulsions were prepared by encapsulation of D-limonene and terpenes mixture and these emulsions were evaluated for their antimicrobial activity against *Lactobacillus delbrueckii*, *Saccharomyces cerevisiae*, and *Escherichia coli*. The parameters taken into consideration were minimum bactericidal concentration and minimum inhibitory concentration and it was found that there was an increase in antimicrobial activity and was influenced by mean diameter and formulation (Donsì et al. 2011).

In another study, the effect of mean diameter and formulation was studied on rate of infusion of carvacrol into food matrices (Donsì et al. 2014). Microcapsules have been found to have excellent protection properties against degradation for encapsulated essential oils and do not influence the antimicrobial activity. In contradiction to that, nanoscale capsules owning to smaller size, passive cellular absorption function may increase leading to reduction in mass transfer resistance. As a consequence, the antimicrobial activity is increased for nanoscale materials and this was witnessed by increase in antimicrobial activity of oils entrapped in liposomes (Gortzi et al. 2007).

Nowadays, wide application of oil-in-water emulsions have been noticed for the protection and delivery of oils, for instance, thyme oil (Wu et al. 2014) and their antimicrobial efficacy is evaluated. Similarly, oil-in-water emulsions are used for encapsulation of essential oil components from clove, lemongrass, thyme and palmarosa and tested for their antimicrobial activity against *Escherichia coli* (Odriozola-Serrano et al. 2014).

Functional nanoemulsions of Eugenol were prepared using sesame oil and surfactants such as Tween-20 and Tween-80 and their antimicrobial efficacy was tested in orange juice system. The study showed that *Staphylococcus aureus* could be effectively inhibited by the nanoemulsion loaded with eugenol (Peng et al. 2015).

Nanoparticles

Nanoparticles use an ingredient has been extensively increased in food industries on account of their physicochemical and functional properties (Joye and McClements 2014). Till date nanoparticles were used profusely in various fields like electronics, medicine and automation. With the experience and knowledge attained from these fields, it can be applied to food science for enhancing food safety (Ravichandran 2010). Nanoparticles of alginate, chitosan and pluronic were combined with nisin and were tested for their antimicrobial efficacy in nutrient broth and tomato juice system. The study confirmed that nano-encapsulated nisin demonstrated greater antimicrobial efficacy compared to free nisin (Chopra et al. 2014).

Usage of peppermint oils has potential benefits such as antifungal and antibacterial properties (Mehri et al. 2015). Essential oils of *Menthapiperita* were encapsulated in chitosan-cinnamic nanogel and tested for their antimicrobial activity and stability against *Aspergillus flavus* and it was found to be effective and inhibit *A. flavus* (Beyki et al. 2014). Chitosan nanoparticles were prepared for encapsulation of polyphenols and tested for antimicrobial activity against various food pathogens and found to more effective against *Bacillus cereus*, *Escherichia coli* O157:H7 and less efficacy was reported against *Salmonella* Typhimurium (Madureira et al. 2015). In case of coatings, metal-based materials with antimicrobial functions are utilized as nanoparticles (Bastarrachea et al. 2015). Silver nanoparticles are enclosed in cellulose pads and kept in contact with beef and tested for microbial load. It was found that the microbial load decreased in the meat extracts (Smolkova et al. 2015).

Nanoparticles of phytoglycogen derivatives were used as carriers of nisin, which represented peptide model and was tested for antimicrobial efficacy against pathogen *Listeria monocytogenes*. The study found that with the degree of substitution of phytoglycogen with β-amylolysis, and octenyl succinate lead to increase the retention of nisin activity for a longer time (Bi et al. 2011).

In most applications including food, nanomaterial synthesis is perceived in two approaches; these are top-down and bottom-up approaches (Nasr 2015). In the bottom-up method, the required nanomaterial is synthesised by building atom-by-atom or cluster-by-cluster. This allows the surface topography to be uniform and can be manipulated very specifically to the required final nanoparticle structure. The top-down approach involves the breakdown of a bulk substance by chemical or physical means to nano-sized particles. Thus, a top-down approach is characterised by surface imperfections (Thakkar et al. 2010). A bottom-up approach is favoured over top-down method as the surface properties are very important to design nanomaterials in the desired way.

Halloysite clay nanotubes were synthesized at ambient temperature by size reduction using high energy ball milling with no specific solvent (Gorrasi et al. 2014). A dilute slurry of cellulose was subjected to high- pressure homogenization to convert it to microfibrillated cellulose. The structure consisted of interconnected microfibrils having diameter in the range 10–100 nm (Herrick et al. 1983). Cellulose nanocrystals were formed from cellulose nanofibres by sulphuric acids hydrolysis (Robles et al. 2015).

Phase separation method, also known as coacervation has been used to form nanoparticles. A study synthesized gelatin nanoparticles by the phase separation method using binary non-solvent system yielding 94 % of particles. A size as small as 55.67 nm in dry state could be achieved by modified coacervation of gelatin (Patra et al. 2016). Cu- chitosan cross-linked nanoparticles were synthesized using ionic gelation approach (Saharan et al. 2015). Chemical methods were used to prepare chitosan nanoparticle by a series of steps- amidation, grafting and cross-linking (Atta et al. 2015).

Films and Edible Coatings

Surface coating method is commonly employed during the fabrication of food packaging films for attaining antimicrobial functions. In order to achieve food packaging materials with antibacterial function, silver nanoparticles coating was suggested. The surface of polyethylene film was modified with corona discharge technique and dipped in silver nanoparticle based colloidal solution. The fabricated nanostructured films were tested for antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* (Sadeghnejad et al. 2014).

With the emergence of nano-encapsulation technique, coating materials are incorporated with nutrients and bioactive agents possessing potential health benefits can be delivered to targeted sites. In second generation coating, use of chemicals, microorganisms or enzymes in coating food surfaces is done which are prone to oxidation and degradation (Falguera et al. 2011).

7.3 Nanoscience in Food Packaging

The packaging criteria required for food is very varied. A very important criterion that a food packaging must accomplish is to provide the necessary barrier properties. Respiring foods like fruits and vegetables will decay-off if the food were to be packed in a packaging material completely impervious to oxygen. Instead, they require a membrane that selectively allows oxygen to enter the packaging, at the same time retains moisture within the packaging material. Non-respiring foods like carbonated beverages have to be stored in containers highly impervious to gas transfer so as to prevent decarbonation of the drink. Not only the sophisticated requirement of food material makes packaging a challenge, the packaging material's behaviour also creates complication in food system (Fig. 7.4). For example, ethylene vinyl alcohol has good oxygen barrier property at low humidity ranges. However, as the humidity goes beyond 75 %, the oxygen transmission rate of ethylene vinyl alcohol shoots up (Duncan 2011).

The behaviour of food cannot be modified as food is expected to be delivered in a fresh state. So the packaging material is to be modified to accommodate the complex characters of food systems. Polymers made into laminates or co-extrudates can obtain suitable barrier properties but recycling them is difficult (Duncan 2011). Polymer nanocomposites are believed to offer a possible solution to the problem of packaging material as the barrier properties of the polymers can be improved by using a single polymer material (polyolefin) or suitable biopolymers (cellulose) intercalated with natural clays in pristine or modified form.

7.3.1 Food Quality

Food quality is associated with food perishability. Perishable products must be stored so as to reduce the loss in food during transportation and storage (Rong et al. 2011). Perishability can be controlled to some extent by carefully monitoring the

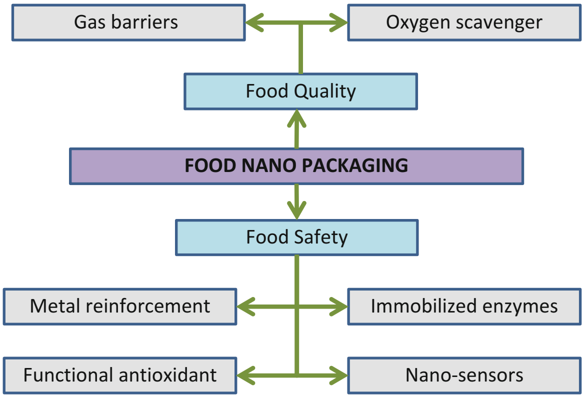

Fig. 7.4 Illustration of nano-packaging in food safety and security

food's exposure to degrading substances like oxygen, light, ethylene (in the case of fruits) and various other factors. Packaging materials are required to contribute to the food quality by influencing barrier properties to form a conclusive food environment.

7.3.1.1 Barrier Properties

The most important property of packaging material is the barrier ability. A suggested technique to tackle the barrier issue is the use of polymer nanocomposites such as silica and clay nanoparticles embedded within the polymer matrix. The primary mechanism by which the permeability of the polymer material is altered is by forcing the diffusant to traverse a 'tortuous pathway' (Bharadwaj 2001). The diffusing material could be oxygen entering the system of packaged material or could be water vapour, carbon dioxide, flavours and other substances entering or leaving the packaging system enclosing the food. In a packaging material consisting of only the polymer material, the diffusing particle would travel a straight unhindered path through the thickness of the packaging material, perpendicular to the surface. By embedding polymer nanoparticles of sufficient aspect ratio, the mean path travelled by the diffusing material is long and undefined, a path described as 'tortuous pathway' as illustrated (Fig. 7.5). The long path buys more time for the diffusing material to diffuse through the packaging material and the effective film thickness increases by the incorporation of nanoparticles in polymers. The nanoparticles thus, embedded into the polymer is called filler while the pure polymer is referred to as matrix. The filler is mostly an inorganic impermeable crystal that

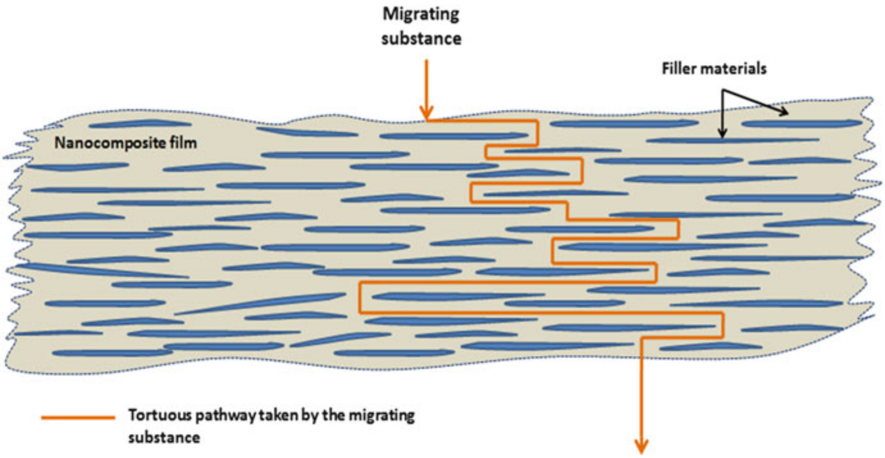

Fig. 7.5 The migrating substance while travelling through a segment of nanocomposite film has to take an undetermined, long and round about path, as the filler material hinders the free movement

makes it necessary for the diffusing material to go around (Duncan 2011). Fillers may include starch nanocrystals (Haaj et al. 2014; Rajisha et al. 2014; Tehfe et al. 2015), chitosan or chitin nanoparticles (Biswas et al. 2015; Chen et al. 2014a; Herrera et al. 2015), carbon nanotubes (Kavoosi et al. 2014; Yu et al. 2014), silicate nano-platelets (Baouz et al. 2015; Decker et al. 2015), silica nanoparticles (Farhoodi et al. 2014; Holt et al. 2014), clay nanoparticles (Bodaghi et al. 2015; Wakai and Almenar 2015) and cellulose-based nanofibres (Ghaderi et al. 2014; Khan et al. 2014a).

The first success story of polymer nanomaterials was that of nano-clays such as montmorillonite. It is naturally formed clay obtained from volcanic debris. This clay has a nano-layered structure, in which layers are spaced by interlayer galleries. In case of montmorillonite, the galleries are bound on either side by silicate layers (de Paiva et al. 2008). Montmorillonite being hydrophilic easily does not solubilise in polymer. This constraint was overcome by the use of alkyl-ammonium group that act as a surfactant and brings down thermodynamic barrier posed by the immiscibility of clay and polymer. Certain other methods have been employed to evenly distribute the clay within the polymer matrix like clay modification and polymer modification with or without the addition of compatible agents. Structures resulting from dispersion of nanoclays into polymer are intercalated nanocomposite, non-intercalated nanocomposites, flocculated nanocomposites and exfoliated nanocomposites. Of the aforementioned probable structures of nanocomposites, exfoliated structure is favoured by researchers due to improved barrier effect and reduced filler loading (Silvestre et al. 2011).

Polylactic acid has been known as a biodegradable polymer. It consists of lactic acid ($CH_3CH(OH)COOH$) monomer units esterified to form the thermoplastic polymer. On a large scale lactic acid is produced from corn starch by fermentation. Polylactic acid films have been commercially used to package 'relatively short shelf life' food in cups, lamination films and overwraps. Cellulose, a widely available nanoparticle forming substance was added to polylactic acid as reinforcement filler material to form the nanocomposite (Herrera et al. 2015). Cellulose was chosen because it was a widely available, low-cost material which permitted high level of polymer filling. Cellulose being hydrophilic, poses difficulty in dissolving with polylactic acid. Therefore, suitable solvent like chloroform had to be employed to cope up with the non-compatibility of polylactic acid and cellulose nanocrystals. Polylactic acid composite films prepared by adding 1 wt.% cellulose nano-crystals exhibited 9 % reduction in oxygen transmission rate and those polylactic acid composite films prepared by inclusion of 5 % cellulose nano-crystals exhibited 43 % reduction in oxygen transmission rate. Surfactant modified-cellulose nano-crystals incorporated film exhibited oxygen transmission rate reduced by 48 % in comparison with unmodified cellulose nano-crystals film. The above findings indicated that cellulose nanocrystals, in pristine and modified forms, could be used to make films with polyvinyl acetate that had improved barrier effect with respect to oxygen. The same result did not hold true for water vapour barrier property (Fortunati et al. 2012).

Biodegradable composite packaging material was prepared from a polymer blend of apple peel powder and carboxymethyl cellulose with different nanoclay reinforcement to improve mechanical and barrier properties of the film (Shin et al. 2014).

7.3.1.2 Oxygen Scavenging Properties

Oxygen is held responsible for most of the deteriorative reactions in food. Be it oxidation of lipids, growth of fungi or proliferation of aerobic bacteria, oxygen is the main degrading agent. It is utmost necessary to eliminate oxygen from food packages so that shelf life is extended. Gas flushing techniques of vacuum packaging and modified atmospheric packaging target controlling the oxygen levels within the sealed packages. However, these techniques do not create a packaged space completely devoid of oxygen due to the fact that the porous food material will hold oxygen and there is permeation of gases through sealed membranes. There came the use of sachets and pads capable of scavenging oxygen within the enclosed space. Oxygen scavenging systems were mostly iron powder based sachets involved in chemical reaction with the moisture within the system (Han 2005; Nakata 2015). It should be noted that scavenging involves chemical or enzymatic reactions to quench oxygen. Sachets posed the problem of accidental consumption with food and their non-compatibility with beverages. Researchers then turned to find other means of putting an oxygen scavenging material inside the package. One such approach is making the packaging film that quenched oxygen and nano-materials seem to have vast potency in this regard (Ahvenainen 2003).

Films co-deposited with nano-crystalline TiO_2, and consequently compressed formed films that could consume oxygen from a packaged environment. TiO_2 required the use of ultraviolet illumination and a sacrificial electron donor, obtained from the organic food for active removal of oxygen. Further, high-pressure compression of the film ensured that the film was non-scattering to light. Good final deoxygenation was observed even when the initial oxygen concentration was very low, indicating that oxygen depletion was feebly dependent on concentration (Xiao-e et al. 2004). Oxygen-sensitive luminophore coated glass beads were used to study the rate of oxygen depletion of film utilizing TiO_2 and UV light. Oxygen scavenging rate of $TiO_2$was found to be 0.017 cm^3 O_2h^{-1} cm^{-2} over a period of 24 h (Mills et al. 2006).

Active packaging films to quench oxygen were prepared using poly (lactic acid) as matrix, modified montmorillonite as filler and thymol as additive. Images obtained from TEM and X-ray scattering patterns convinced the existence of an intercalated structure that improved mechanical properties and oxygen barrier properties. Thymol addition brought good antioxidant property to the packaging material in addition to superior physical properties, thus bringing forth promising active packaging material (Ramos et al. 2014).

7.3.2 Food Safety

In the past few decades food safety has become a major concern all around the world. Recent consumer demand for organic food is the evidence that consumers are careful about the food they consume. Microbial safety is very crucial to develop trust among the consumers that the packed food is safe for consumption (Grunert 2005). Foodborne diseases and safety issues was estimated to affect the US economy by $77.7 billion annually (Hakovirta et al. 2015). The recent food safety ideas involve control of food-borne microbes affecting humans and continuous surveillance (Fox et al. 2015). Antimicrobial nanocomposites and nano-laminates aids in preventing pathogen multiplication while nanotracers and nanosensors assist in tracking the product safety.

7.3.2.1 Nanocomposites

Nanocomposites filled with metal nanoparticles are known to possess antimicrobial property and the most promising results have been obtained by the inclusion of silver nanoparticles. Gold and zinc nanoparticles are also studied for their antimicrobial function (Silvestre et al. 2011; Maddineni et al. 2015).

Silver is known to be a wide spectrum antibacterial. It has been found to be effective against a large range of bacteria, algae, fungi and some viruses. With the progressing trend of development of resistance by microbes against several molecular antimicrobials, research suggests that silver is very potent antimicrobial (Duncan 2011). Mechanisms that account for silver's bactericidal effect include mainly the ability of silver to bind with oxygen, nitrogen and sulphur atoms of functional species present in biomolecules; the result may be cell wall damage and cell fluid loss. Silver may also bind with proteins including enzymes and affect the normal metabolism of the bacterial cell (Dasgupta et al. 2016b, c). Cell reproduction may be hindered if silver interacts with DNA, which accounts for bacteriostatic effect (Cavaliere et al. 2015). The cytotoxicity level of silver ions per litre of water is 10 mg. When such is the case, a concentration as low as a few micrograms of silver ions are capable of destroying bacteria present in water (Damm et al. 2008).

Studies have indicated that when silver was filled into polyamide-6 (nylon/polycaprolactam, a polymer) in nanoparticle form exhibited more bactericidal effect than the same polyamide filled with silver microparticle. This effect was justified by the fact that nanosilver held larger surface area and so the release of silver was higher. Also, the study discovered that 9.5×10^{-4} mg l^{-1} cm^{-2} day^{-1} of silver release could eliminate *E.coli* totally in 24 h (Damm et al. 2008).

The chemical behaviour of silver ions was held responsible for the antibacterial property of silver. The inability of silver nanoparticles to be harmless to silver resistant strains of *E. coli* supported the belief that silver nanoparticles were mere delivery vehicles of silver ion. This theory was in opposition to the another research which found silver nanoparticles to be effective against of *P. mirabilis* and *E. coli*, both silver resistant organism (Duncan 2011). There may be other factors affecting the antimicrobial activity of silver like the presence of salts, continuous ion release, size, shape and much more (Kim et al. 2007). Antimicrobial nanocomposite films from chitosan- gold nanoparticles and chitosan- silver nanoparticles were prepared and the microbial destruction was studied against gram positive bacteria, gram negative bacteria, fungi and yeast (Youssef et al. 2014).

Extensive research over the killing of microbes by using Titanium dioxide started following the findings of Matsunaga in 1985 (Mirhoseini and Salabat 2015; She et al. 2015; Ranjan et al. 2015, 2016). Matsunaga and the associated team had discovered that near UV activated TiO_2–Pt catalyst was capable of microbes present in water. Several researches followed this finding to explore the antimicrobial effect of photoactivated TiO_2 against numerous fungi, algae, bacteria, viruses and cancer cells (Kim et al. 2003). Most of the researches, even today try to combine photoactivated TiO_2 and other antimicrobials like silver to achieve effective antimicrobial action in a film or coating.

Nano-TiO_2 doped with Ag and iron and modified by using methacryloxypropyltrimethoxysilane was used to prepare a multifunctional fluorocarbon coating. Research showed that such a modified film exhibited an antimicrobial property of 92 % if activated using light. The bactericidal ability was attributed to a variety of combined factors that included quantum of TiO_2, light doses and effects of doping materials (Wang et al. 2010).

Semiconductor-metal composite nanoparticles formed from TiO_2 semiconductor and doping metals like vanadium and gold were dispersed in solution. This solution formed by sol-gel method was claimed as antimicrobial (with killing efficiency of 60–100 %) coating against the organisms studied, which are, gram-negative *E. coli* and gram-positive *Bacillus megaterium*. General techniques employed for studying nanoparticles include transmission electron microscopy, atomic force microscopy, X-ray diffraction and some spectroscopic methods (Fu et al. 2005).

Several studies have indicated that TiO_2 on photocatalysis achieves microbial killing by the formation of reactive oxygen species like O_2 (superoxide anion radical) and $\cdot OH$ (hydroxyl radical). These free radicals cause mineralisation by reacting with organic compounds of membrane and cell wall of the pathogens, resulting in death (Foster et al. 2011). Nano size just seems to accelerate this antimicrobial effect of TiO_2 by exposing more active sites due to a high surface area that favors catalytic reactions (Fu et al. 2005). Deacetylation of chitin forms chitosan, a positively charged natural biopolymer that is non-toxic. Chitosan nanoparticles, in conjunction with Ag (Pinto et al. 2012), Cu (Pinto et al. 2013; Qi et al. 2005) and clay nanoparticles (Rhim et al. 2006), have been attempted to prepare food compatible films with cytotoxic ability. The mode of action of chitosan is suggested that cell membrane is disturbed causing rupture of the cell due to the interactions between chitosan and cell membranes that possess opposite charges (Qi et al. 2004). A comparative study performed to compare the antibacterial effect of chitosan/cellulose and chitosan/cellulose–AgNPs nanocomposite films indicated that chitosan in association with silver nanoparticles performed better in terms of antimicrobial activity compared to just chitosan/cellulose film (Lin et al. 2015).

Nisin has been attempted to be incorporated into nanocomposite films to make it a functional film. In a poly lactic acid-cellulose nanocrystals nanocomposite system nisin was reinforced using the method of adsorption coating to inhibit the propagation of *L. monocytogenes* in sliced cooked ham (Salmieri et al. 2014). In a similar meat system, experimented with nisin immobilized cellulose nanocrystal embedded chitosan films increased the lag phase of *Listeria* (Khan et al. 2014b). The matrix forming materials of nanocomposites like food-grade montmorillonite readily pick up nisin into the interlayer space of the clay as indicated by X-ray powder diffraction studies (Meira et al. 2015). Immobilized systems prepared using montmorillonite intercalated with nisin were found to have bactericidal activity against *Enterococcus faecium* C1 (Ibarguren et al. 2014). Nanocomposites with montmorillonite and nisin at less than 5 % (w/w) in a polypropylene film could inhibit gram- positive *Staphylococcus aureus*, *Listeria monocytogenes* and *Clostridium perfringens* (Meira et al. 2014).

In another study, two types of nanoclays were used to deliver essential oils like thymol, eugenol and carvacrol by blending with linear low-density polyethylene to form nano-composite films. The layered structure of the first nano-clay, montmorillonite allowed the loading of essential oil on the interface and tubular structure of a second nano-clay, halloysite allowed filling into the nano-channels. Tween 80, a food grade surfactant assisted the loading of nano-clays with antimicrobial oil. Such nano-reinforcement made the packaging material active and enabled delivery of the antimicrobial essential oils over a prolonged period in meat-based food system (Tornuk et al. 2015). Halloysite nano-tubes were described as nano-containers owing to their ability to hold model antimicrobial sodium benzoate, with the nanotubes embedded within a Poly (ethylene terephthalate) matrix. High chemical loading, around 1–7 % was achieved within halloysite nano-clay tubes by using simple procedure, thus, eliminating the need for hazardous chemicals. This study indicated that antimicrobial composite packaging had its bactericidal effect for prolonged time when loaded into halloysite as compared to the antimicrobial release after simple dispersion of active compound into the polymer matrix (Gorrasi et al. 2014).

A novel filler material, microfibrillated cellulose was made from blue agave bagasse to check the release of natural antimicrobial lysozyme and was incorporated into polylactic acid polymer matrix after modification. In this study, the ability to retain lysozyme associated with the microfibrillar cellulose by the probable hydrogen, electrostatic and ion-dipole interactions was analysed by fitting the diffusion data with Fick's law (Robles et al. 2015). The amount of antimicrobial required to bring about effective killing of microorganisms is considerably less when the size of antimicrobial agent, eg, chitosan, benzoic acid and sorbic acid, is reduced to nanoparticle size. The author proposes their potential for applications in smart and active packaging (Cruz-Romero et al. 2013).

7.3.2.2 Nanolaminates

Nanolaminates, with regard to food packaging, refer to several layers of edible film coatings applied over food itself or polymer/surface with the layers bonded together by physical or chemical interactions. It is mandatory for the film so formed to lie within the nanometre range of 1–100 nm for the laminate to be called a nanolaminate. The edible substances used for coating include polymers of carbohydrate, protein and lipid. Nanolaminates of precise thickness are formed by 'layer by layer' deposition technique (Ravichandran 2010). This technique uses polyelectrolytes like polysaccharides and proteins (Mishra 2012) to be deposited on the prepared surface by making use of electrostatic interaction (attraction between the opposite charges) or similar interactions and thus, holds the multiple layers intact. In actual practice, the formation of nanolayered structure is achieved by spraying the layer forming material and then washing, and again spraying and washing, until the required number of layers is formed. In an alternate method, cyclic dipping and washing are used to form the specified nanolayers. A number of functional compounds like flavours, antimicrobials, colours and antioxidants can also be incorporated into the nanolaminate film (Weiss et al. 2006).

Polysaccharides, namely sodium alginate and chitosan were used to form a laminate made of five layers through layer by layer deposition. The laminate coating was made over aminolyzed/charged polyethylene terephthalate film with the objective of improving the water vapour permeability and mechanical property. One of the alginate layers had a thickness of 19.55 nm. The water vapour permeability of the laminated film was $(0.85 \pm 0.04) \times 10^{-11}$ g^{-1} s^{-1} Pa^{-1} and the hardness raised by 0.245 ± 0.06 GPa (Carneiro-da-Cunha et al. 2010). Polysaccharide nanolayers had significantly contributed to improve the barrier properties of the nanolaminated film. The general opinion is that polysaccharide and protein polymers form a coating that has good gas barrier property but poor water barrier ability. On the other hand, lipids being hydrophilic are good moisture barriers but lack the necessary gas barrier capability (Weiss et al. 2006).

Lipids can also be used as nano coatings. In a study lipid nanolayer was formed over a hydrophilic film made up of starch. Sunflower oil could be coated over the starch film due to favourable interfacial interactions. In nanolaminated films it was found that permeation phenomenon is reduced and that coefficient of water diffusion had dropped down considerably for the oil laminated film when compared with the corresponding starch film (Slavutsky and Bertuzzi 2015).

Immobilisation of antimicrobial on food contact surface is another approach that nanoscience takes for improved safety of food. Nanoemulsion based edible coatings were prepared using lemon grass oil as a preservative and compared with the edible coatings prepared from conventional emulsion on fresh-cut Fuji apples. Nanoemulsion based coating performed better coating at a concentration of 0.1 % lemongrass oil. It inhibited the natural microflora and slowed the proliferation of psychrophilic bacteria for a storage period of 2 weeks (Salvia-Trujillo et al. 2015).

A 15 layer film was fabricated using edible protein hen egg white lysozyme and poly (L-glutamic acid) by layer by layer deposition. Thickness per layer in the study was 1–10 nm. The model organism *Microccocus luteus* in the ambient liquid medium was inhibited by lysozyme immobilized in the laminate (Rudra et al. 2006). Biopolymer- based mats were fabricated using electrospinning technique that consists of nano-fibres with unique functions. In food sector, they could be manipulated for preparing transparent barriers and active packaging of preservatives (Torres-Giner 2011). On a template of nanofibrous mats, lysozyme-pectin bilayers were coated and antimicrobial ability was tested (Zhang et al. 2015). Inhibition against *Escherichia coli* and *Staphylococcus aureus* were observed by the immobilization of lysozyme and gold nanoparticles. The strong attractive interaction between negatively charged gold nanoparticles and positively charged lysozyme favoured their layer by layer assembly on negatively charged cellulose nanofiber mat (Zhou et al. 2014). Cinnamaldehyde formed into nano-liposomes by using polydiacetylene-N-hydroxysuccinimide bilayers were immobilized on glass surfaces. The study showed evidence of antimicrobial activity of immobilized cinnamaldehyde against *Escherichia coli* W1485 and *Bacillus cereus* ATCC 14579 (Makwana et al. 2014).

7.3.2.3 Nano-biotracers

Food safety issues of the recent days have led to increased tracing methods along the food supply and distribution channel. Food traceability is necessary edible substances like for grains and processed food (Ceruti et al. 2006). Food product may move a long and complex path from farm to customers. When such is the case, food traceability ensures that the product is identified with respect to origin and quality. Such an identification system creates trust in customers. Traceability also ensures that the producers take their responsibility seriously (Ceruti et al. 2006). Barcodes and radio-frequency identification are the popularly used identification tags. The radio-frequency identification tags were found to be not very economical (Véronneau and Roy 2009), while the bar codes suffer the possibility of being erased off leading to non-readability. Nanotechnology opens new gates in product identification and tracking by putting forth the technology of nanobarcodes.

Machine-readable sub-micron sized tags called nanobarcodes have been developed for use as identification devices in many applications including tracing food along the supply chain. These ID devices are durable and must be encoded to use. The structure of nanobarcode is mostly a cylinder with length 0.04–15 mm long and the diameter between 20 and 500 nm. Nanobarcodes are made by electroplating inert metals like gold, silver, platinum and nickel over templates of pre-defined size and the formed nano-rods are released into suspension from templates (Warad and Dutta 2005).

Nanobarcodes made up of different segments were fabricated. A magnetic and non-magnetic segment over a single nanowire will allow both magnetic and optical responses to be produced by the barcode, thus improving the detection capability. The template used to manufacture the nanobarcode was anodised aluminium oxide membrane as this membrane has nano-channels. Two segments of the barcode, one of CoFe (an alloy) and the other segment of Au were fabricated on a single barcode using one-bath pulsed electro-deposition. Electron microscopic images of the so formed nanobarcodes exhibited well-differentiated interfaces between segments (Yoon et al. 2012).

Along with appropriate detection and storage devices, nanosensors can be used as a quality assurance technique by tracking the food microbes, heavy metals and harmful chemicals. For assurance of safe produce, the sensors can help by detecting, capturing and recording process and storage condition along the path of processed food. Even low-cost nanosensors can be inserted into every package to monitor quality up to consumption during long shipments especially in cases of highly perishable food commodities, for example, prevention of temperature abuse (Neethirajan and Jayas 2011). Nanosensors in food are basically miniature biosensors. A biosensor consists of a biological recognition component, referred to as bioreceptor. This bioreceptor is linked to a transducer. The receptor conceives the analyte of interest and forms electronic signal, enabling the measurement of the analyte of interest (Viswanathan and Radecki 2008). Nanosensors have been studied for various sensing applications including detection of microbes, toxins, pesticides, volatile compounds and gases like oxygen and carbon dioxide.

Microbial detection is generally done by plating techniques and only these are considered reliable *E. coli* was detected by a sensor that used streptavidin-coated ferrofluid (Fe_3O_4) nanoparticles to amplify the feeble frequency change produced in the probe while detection. The probe had a single-stranded DNA (ssDNA) as receptor connected to transducer. The signal obtained had a quantitative relation with the *E. coli* concentration. The improved sensitivity was associated with large mass of nanoparticles compared with DNA targets (Valdés et al. 2009).

Hexanal is a volatile compound that indicates oxidation in food. A novel method to detect even minute concentrations of hexanal was devised which was olfactory-nanovesicle-fused carbon nanotube-transistor biosensor. It was meant to mimic the canine olfactory senses to detect hexanal precisely without confusing with similar volatile compounds like heptanal, octanal and pentanal. Its construction was done by mounting receptor on carbon nanotube channel, in which conductance change was produced when hexanal contacted the receptor. Concentration as low as 1 fm was detected by this sensor (Park et al. 2012).

Pesticide detection is achieved by nanosensors meant for organophosphorus pesticides by the use of up conversion nanoparticles and gold nanoparticles. Very low levels up to 0.67, 23 and 67 ng/L were achieved for organophosphorus pesticides-parathion-methyl, monocrotophos and dimethoate, respectively (Long et al. 2015). The up conversion nanoparticles are a new range of fluorescent nanomaterials that work by converting infrared radiations to visible light (Wang et al. 2011). Several researches have attempted to make nanosensors for oxygen detection as well.

Gas detection is possible by measuring resistivity changes of carbon nanotubes in response to the adsorption of gas molecules on them. Carbon nanotubes consist of a single layer of cylindrical graphene sheet. Since every atom of a graphene sheet is a surface atom, detection of least levels of gas becomes theoretically possible

(Vanderroost et al. 2014). Carbon nanotube was made to transfer charge due to the adsorption of NH_3 and it was found to be influenced by environmental oxygen (Peng et al. 2009). Several detectors based on carbon nanotubes were attempted to prepare for identification of trace levels of SO_2, H_2, H_2S, O_2, CO_2, SO_2 and other organic compounds (Kauffman and Star 2008). Hindrances from contaminants during detection of a specific gas is an issue to be addressed (Vanderroost et al. 2014). Electro-catalytic activity of cobalt nitroprusside nanoparticles had improved even in a matrix consisting of interfering organic and inorganic, ions and acids when prepared by drop by drop method. This electrochemical behavior helped the quantification of sulphite in water and food at trace levels (Devaramani and Malingappa 2012).

7.4 Nanotechnology in Agriculture and Food Industry

The public perception of food derived from nanotechnology is similar to that of GM foods as the consumer needs to be explained clearly the advantages of opting nanotechnology engineered foods. A survey was done to record the view of public whether they would opt a food (tomatoes) protected by a nanostructured packaging material or a food which itself is nano-engineered (bread fortified with nanocapsules of omega-3 fatty acids). The survey suggested that public would opt for a food wrapped in nanostructured packaging material rather that of nano-engineered food (Sozer and Kokini 2009).

Extracellular secretions of *Aspergillus fumigatus* TFR-8 were used in the production of ZnO nanoparticles (Fig. 7.6). Effect of these biologically transformed ZnO nanoparticles on clusterbean (*Cyamopsis tetragonoloba* L.) was investigated to increase the amount of native phosphorous mobilizing enzymes. It also enhanced the gum content in beans by 7.5 % indicating that ZnO nanoparticles can be used in industrial and medical applications along with agricultural sector A significant increase in the root and shoot length was found i.e. 66.3 % and 31.5 % respectively (Raliya and Tarafdar 2013).

Researchers indicate the possible hazards that can occur when the nanoscale materials will interfere with the environment. Literature survey reveals the possible risks associated with the exposure of engineered nanomaterials to the environment as well as their reaction in human digestive tracts (Chen et al. 2014b). Researcher's main goal is to understand the behaviour of these nanomaterials and do detailed risk assessment related to them so that on can distinguish between the engineered nanomaterials and its background particles and investigate the level of toxicity due to these products. Debate is on among researchers to make these engineered nanomaterials sustainable and safe (Koelmans et al. 2015).

Future prospects include study of models for the prediction of the interactional effects of engineered nanomaterials with living cells and tissues (Oksel et al. 2015). The use of nanomaterials in agriculture is reviewed. Its effect on the plants and the produce from it is investigated. A research conducted in this aspect showed that when sand was mixed with silver nanoparticles and wheat plants were grown on it,

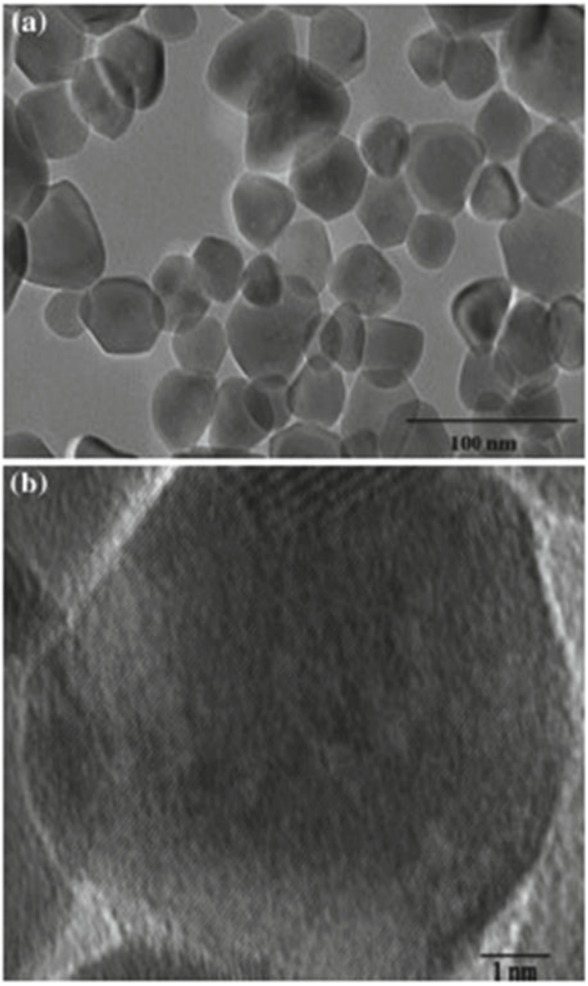

Fig. 7.6 TEM image of ZnO nanoparticles

the result was found to decrease in the growth of shoots and roots with respect to given dose (Dimkpa et al. 2013).

MgO nanoparticles (Fig. 7.7) synthesized from *Aspergillus flavus*, strain TFR-12 was used to study its effect on the chlorophyll content present in the leaves of Clusterbean (*Cyamopsis tetragonoloba* L.). A detailed study of reports suggested significant improvement in growth of shoot-root length (18.2–49.2 %). MgO nanoparticles were found to be phenomenal for the enhancement of chlorophyll photosynthetic pigment by 76.1 % at a concentration of 15MgL^{-1} (Raliya et al. 2014). The combined effect of Cu-chitosan nanoparticles (Fig. 7.8) on the growth

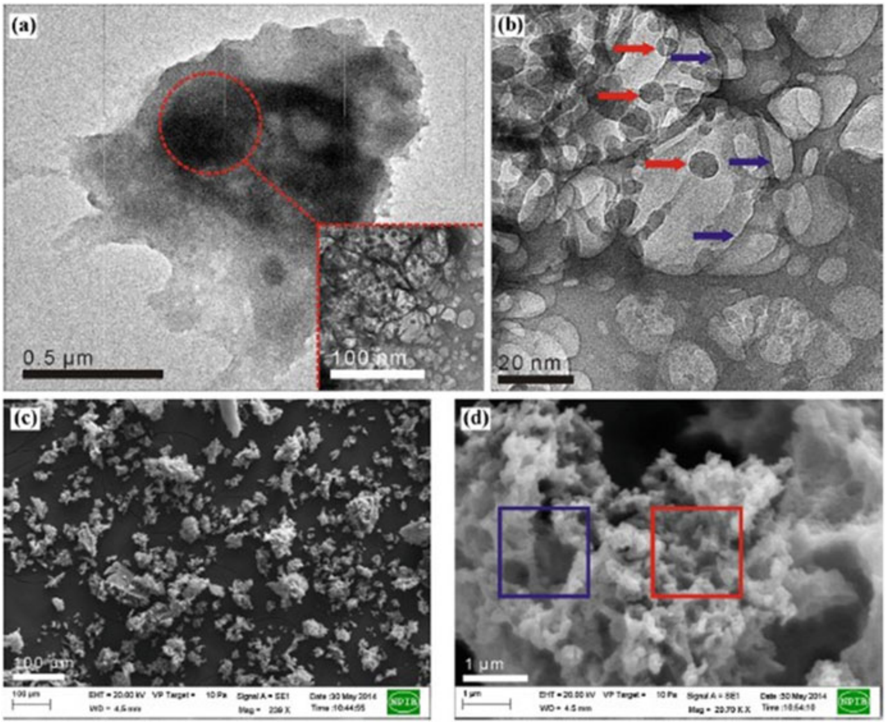

Fig. 7.7 TEM image of MgO nanoparticles

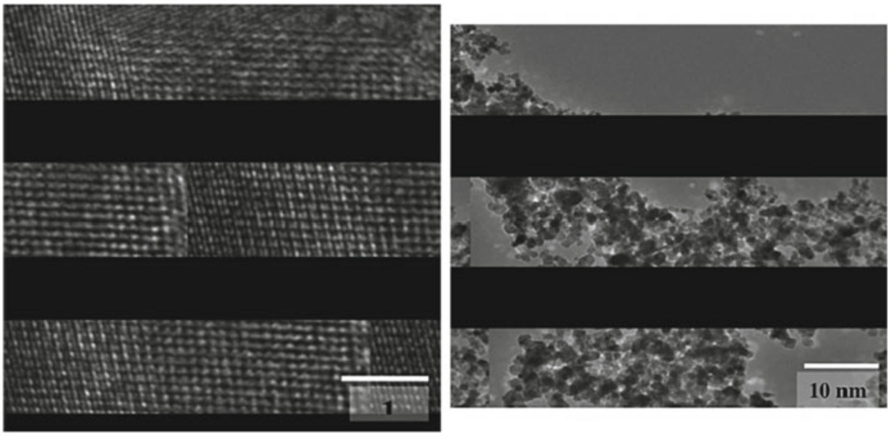

Fig. 7.8 TEM images of Cu-chitosan complexes

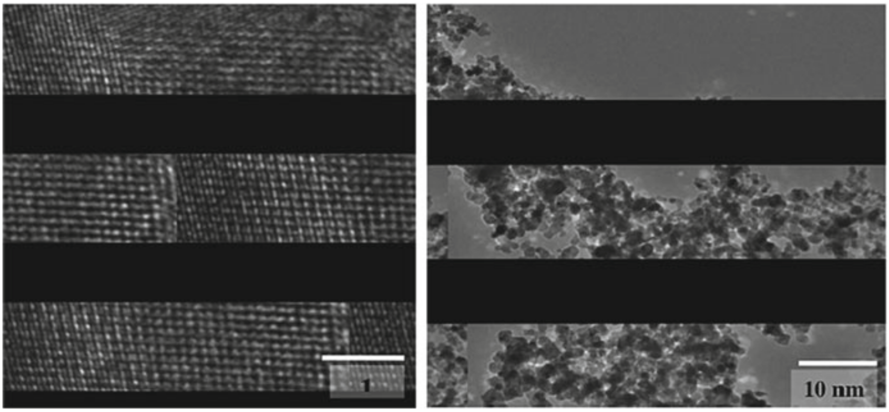
[redacted] [redacted] [redacted] [redacted]

Fig. 7.9 TEM images of TiO_2 nanoparticles

promotion and anti-fungal efficacy of tomato was studied and it was found to enhance various factors such as seed germination and seedling length and exhibited significant antifungal property (Saharan et al. 2015).

Biosynthesized TiO_2 nanoparticles (Fig. 7.9) was found to have many benefits such as procured at low cost and is eco-friendly in nature, as it is produced from *Aspergillus flavus* TFR 7. Influence of characterized TiO_2 nanoparticles on mung bean was investigated and it was found that it increased the shoot length and root length by 17.02 % and 49.6 % respectively (Raliya et al. 2015). Concept of green nanotechnology should be implemented for controlling the treatment and risk associated with nano-engineered products and can lead to sustainable development (Bergeson 2013).

7.5 Regulatory Aspects

Regulations for nanotechnology are widely framed in many countries (Takeuchi et al. 2014; Jain et al. 2016). Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals in the European Union is the main regulation body that covers nanotech-derived materials (Parliament and Union 2006). European commission has recognized nanotechnology as one among its major six key enabling technologies that significantly contribute for development of industrial sectors (Parisi et al. 2014). Discussions on the definition regarding the size range of nanoparticles in between 1 and 100 nm is being reviewed (Rauscher et al. 2012). There are wide ranges of nanotechnology produced food products which are available in global market but are not confining to safety testing standards. Thus, there is a dire need of toxicological research and risk assessment in food sector. Current toxicity testing standards which are approved for conventional foods can be used as a base regulation for drafting the toxicity testing of nanotech-derived food products. However modifications are required to be done as greater difference occurs between conventionally produced materials and nanomaterials (Cushen et al. 2012). US has the largest nano products in the global market when compared to Europe and East Asia (Chau et al. 2007). Currently, the negative impacts of nanotech-derived food products on public health is unclear and thus proactive measures are taken to dictate precautionary terms so as to limit the toxicity of nanomaterials. In order to fill the knowledge gap, more research studies supporting the safety of nano-derived foods are yet to be proved and a through risk and benefit analysis is the needed for proactively avoid upcoming unpredicted health hazard. In another study it is observed that public opinion about nanotechnology and its derived products is not negative if they are clearly explained regarding the benefits of opting them (Parisi et al. 2014).

7.6 Toxicological Effects of Nanomaterials

As nanomaterials have a high surface area they are presumed to have large toxic effects when compared to bulk materials, although no evidence has been recorded as such regarding the potential negative impacts of using of nanomaterials in food packaging. A detailed research on the effect of nano-engineered food on the microbial flora of mouth and gut is required to know the risk associated with it and update the current regulations (Sozer and Kokini 2009). Food products containing engineered nanoparticles are launched into the global market, yet the consumers are completely unaware of their properties and behaviour (Chen et al. 2006). In spite of lacking strong regulations to vigil the production and risk assessment of these nanomaterials, notable food products containing additives of nanoscale are being circulated in the global market namely iron, phytochemicals and zinc oxide in the case of nutritional drinks, oils and breakfast cereals, respectively (Sozer and Kokini 2009). A recent survey states that nanotech foods are applied almost in all food application fields and draws more attention for having a regular check of toxicology. Even though health benefits are claimed for nano-engineered foods, little attention has been paid to acknowledge the risk assessment due to toxicity and potential threats of nanomaterials (Bouwmeester et al. 2009). In case of agricultural sector, the nano-engineered fertilizers and pesticides are presumed to post health risk to small farmers (Dasgupta et al. 2015).

Even though US Food and Drug Administration legislates the manufacturers to declare their product to be free from harmful additives, this does not specifically cover nanoparticles which draw thought of safety of nano engineered foods (Sozer and Kokini 2009). Knowledge on the physicochemical properties of nanoparticles is a prerequisite to know the toxicity caused by it, as variation in toxicity between particulate and nanoscale materials has been witnessed. There is need for the regulatory bodies to dictate strict terms and regulations to the manufactures of nano engineered foods. As a result the foods claiming false allegations of being "Nanotech foods" will be minimized in market. Instruments and human intervention is required for verification and validation of nano-products (Bouwmeester et al. 2009).

7.7 Conclusion

There is an unlimited number of applications of nanotechnology in processing and packaging of foods. Nanotechnology has already entered the packaging world with improved physical and mechanical functionality; however use of nanotechnology in active packaging and tracking is being researched actively. Nanotechnology has a greater potential in food processing in terms of using nano-structured ingredients as delivery systems for improved delivery of nutrients or antimicrobials to create a new generation of health foods with better retention of key nutrients and natural flavours with added safety against food pathogens. Significant research is already in progress toward improved processing and packaging of food by the discovery of new nanostructures with novel functionalities. Lastly, nanotechnology has also shown promising applications in delivering novel methods of real-time food quality and safety indicators for improved consumer confidence. Needless to say that nanotechnology will soon be encompassing all aspects of the food manufacturing industry.

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Chapter 8
Nanomaterials for Soil Fertilisation and Contaminant Removal

Mrudula Pulimi and Sangeetha Subramanian

Abstract Expanding population and increasing consumption is inducing higher pressure on agricultural resources and food production. Agriculture depends to a large extent on the quality of soil and water resource availability. Soils should ensure water retention, provide sufficient nutrients and not contain any contaminants. However, anthropogenic and natural factors are responsible for the deterioration of soil quality in the form of erosion, loss of water retention capacity and nutrients, and contamination. Large scale use of agrochemicals in the form of fertilisers and pesticides has given rise to increase in the levels of contaminants in soil and ground water. Here we review the application of nanomaterials to improve nutrient quality and to remove soil contaminants. Nanomaterials such as nanoclays, nanozeolites and nanominerals have been used to enhance water retention and as nutrient carriers. These nanomaterials promoted seed germination, plant growth, phosphorus and nitrogen fixation, versus conventional methods. Nanoparticles have also been used for remediating soils contaminated by herbicides, pesticides, organic pollutants and heavy metals. Conventional soil remediation methods such as phytoremediation, thermal treatment and electrokinetic degradation, have been improved using nanoparticles.

Keywords Nanoremediation • Contamination remediation • Soil quality • Sustainable agriculture

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8.1 Introduction

Material with particle size of nanometer ranging between 1 and 100 are considered as nanoparticles and any technology that deals on nanoscale means nanotechnology. The growth of nanotechnology has considerably inflated its application of nanomaterial in different area (Khot et al. 2012). Different engineered carbon based nanomaterial (single and multi-walled carbon nanotubes), metal (quantum dots, nanogold, nanosilver) and metal oxide (titanium oxide, zinc oxide and cesium oxide) based nanomaterial, nano sized polymer material called dendrimers and nano composites material are built for different functional properties. The major advantages of nanomaterial over bulk material include decrease in melting point and surface area, increase in dielectric constant and mechanical strength (Nagi et al. 2012; Maddineni et al. 2015; Dasgupta et al. 2016a, b; Ranjan et al. 2016). In addition, size of nanoparticles enables them to absorb exceptionally on to other material (Nagi et al. 2012; Dasgupta et al. 2015; Ranjan et al. 2014, 2015, 2016). Because of all these unique behaviour and properties, nanoparticles have wider application in textiles, clothing, and cosmetics, pharmaceutical, electronic and paint industry. Also they are widely used for development of health care products and remediation of contaminated environment. In addition to its wider application in major industries, nanomaterials are also applied for the prospects of agriculture in several ways (Jain et al. 2016; Baruah and Dutta 2009; Handford et al. 2014; Sastry et al. 2010; Taghiyari et al. 2015; Dasgupta et al. 2016c). Figure 8.1 represents some of the applications of nanomaterials in different fields.

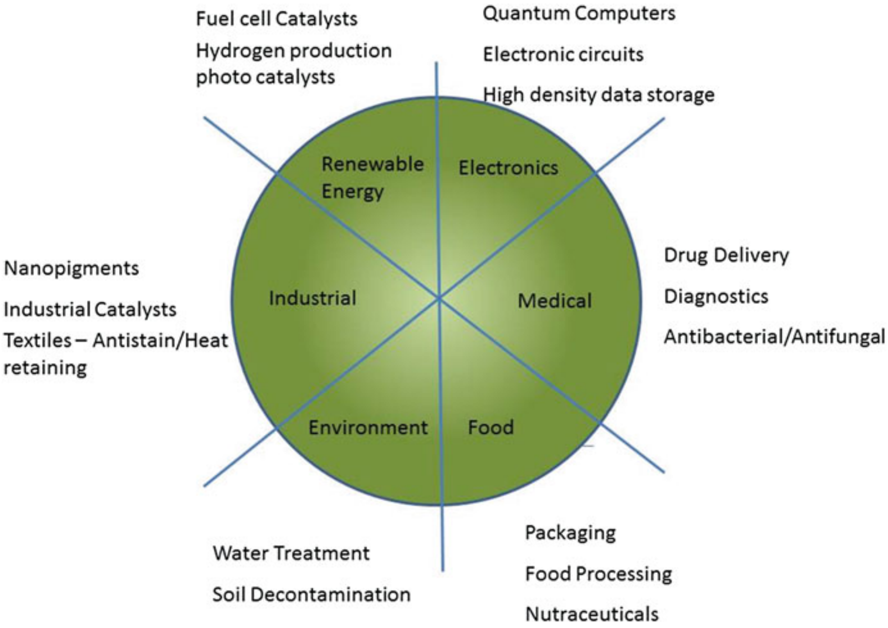

Fig. 8.1 Applications of nanomaterials in various fields

Escalation of human population has led to decrease in productive land to less than 11 % of total earth area (Mermut and Eswaran 2012). With limited availability of resources, development in agriculture has to be attained by increasing the fertility of a soil. Although conventional soil management methods are available, nanotechnology is reported by many researchers currently as an alternate technology for sustainable soil management. Fertility and quality of the agricultural soils primarily depends on quality and quantity of water available, micro and macro nutrients present in the soil. The depletion of nutrient quality in soil is predominantly caused due to man-made or natural soil erosion and accumulation of toxic pollutant in the soil. This paper reviews on application of different nanomaterials for improvement and remediation of soil.

8.2 Soil Amendments

Soil amendments are materials used to improve the physical properties of soil such as water retention capacity, nutrient availability, structure, drainage in order to produce better crop yields. Several soil amendments have been in use historically as fertilizers and soil conditioners. The purpose of fertilizers is to provide adequate nutrients for plant growth. Whereas, soil conditioners have minimum nutrient concentration but are added to enhance the biological, physical or chemical nature of soils. The indiscriminate and ineffective use of soil amendments can lead wastage of nutrients, hence nanotechnology was proposed to enhance the effective use of nutrients. The application of nanotechnology for agriculture includes (i) nanomaterials as enablers for delivery of agrochemicals (ii) sensors to monitor plant stress and soil conditions and (iii) improvement of plant traits against environmental stress and plant diseases. In this review, we will discuss about nanoparticles which are specifically used as nanofertilizer or as carriers for fertilizers. A summary of various types of nanomaterials used as soil amendments is given in Table 8.1.

8.2.1 Nanoclays

Clays are an integral part of soil mainly consisting of phyllo-silicate minerals with varying water retention capacities. Clays offer high surface area and have a net negative charge which helps clays in retaining plant nutrients and act as a pH buffer in soil. Clays lose their plasticity and become brittle when the water content is reduced. Nanoclays are generally prepared from the smectite group of clays which includes montmorillinate. Nanoclays have been extensively used in preparing polymer nanocomposites which have been applied in paints, cosmetics, drug delivery and water treatment. Nano-clay polymer composites have also been used as nutrient carriers for enhancing plant growth and for enhancing the water retention capacity of soils.

Table 8.1 Nanomaterials used as soil amendments

Type of nanomaterial	Purpose	Reference
Polymer nanoclays	Slow release of nitrogen and phosphorus	Sarkar et al (2013, 2014, 2015)
Poly(acrylamide-co-acrylic acid)/$AlZnFe_2O_4$ superabsorbent hydrogel nanocomposite	Water retention	Shahid et al. (2012)
Acid phosphatase immobilized on nanoclays	Phosphorus mineralization	Calabi-Floody et al. (2012)
Phytase immobilized on nanoclays	Phosphorous mineralization	Menezes-Blackburn et al. (2014)
Nanoporous zeolite	Nitrogen release	Manikandan and Subramanian (2014)
Nanocomposite PAAm/methyl cellulose/montmorillonite hydrogel	Carrier for urea	Bortolin et al. (2013)
Nanozeolite based urea	Nitrogen release	Thirunavakkarasu and Subramanian (2014)
Aminopropyltrimethoxysilane-zeolite based urea	Nitrogen release	Hidayat et al. (2015)
Carbon nanoparticles	Water retention	Saxena et al. (2014)
Magnetite (Fe_3O_4)	Growth of ocimum basilicum	Elfeky et al. (2013)
Hydroxyapatite	Growth of chickpea	Bala et al. (2014)
Nano hydroxyapatite	P fertilizer	Montolvo et al. (2015)
Nano-hydroxyapatite	To resist Cd stress in Cd contaminated soils	Li and Huang (2014)
Urea-modified hydroxyapatite nanoparticles encapsulated wood	Slow release N fertilizer	Kottegoda et al. (2011)
Nanosilica	Nutrient	Karunakaran et al. (2013)
Nano silica	Silica availability and biomass content of soil	Rangaraj et al. (2014)
Nano silica	Silica fertilizer	Suriyaprabha et al. (2012)
Mesoporous silica nanoparticles with urea	Urea	Wanyika et al. (2012)
Nano Zn	Growth of pearl millet	Tarafdar et al. (2014)
Zn encapsulated in Mn core shell	Zinc	Yuvaraj and Subramanian (2014)
ZnO nanoparticles	Zinc and phosphorus uptake	Watts-Williams et al. (2014)
Nano iron, phosphorus and potassium	Fertilizer for saffron flowering	Amirnia et al. (2014)
Nitrogen fertilizer and nanocarbon	Nitrogen use in saline-alkaline soils	Fan et al. (2012)
Nano TiO_2	Phosphorus uptake	Hanif et al. (2015)
NanoN_2 chelate; sulfur coated N_2 chelate	Nitrogen release	Zareabyaneh and Bayatvarkeshi (2015)

A series of nanoclay-polymer composite nutrient carriers were prepared by the reaction of different types of clays such as kaolinite, mica and montmorillonite with partially neutralized acrylic acid and acryl amide with N,N-methylene bisacrylamide as a crosslinker and ammonium persulfate as an initiator. Six different types of nanoclays were used with different types of clays with and without amorphous aluminosilicate. Among the different nano-polymer composites, the percentage release of nutrients at 48 h ranged from around 70 % in the polymer/clay (montmorillonite) composite to 90 % in the polymer/clay (kaolinite) composite proving that these nanoclays can be utilised for slow release of nutrients. Further the nanopolymer composites were loaded separately with di-ammonium phosphate and urea solution. Release of phosphorous and total mineral nitrogen from the polymer composites loaded with diammonium phosphate and urea, respectively, were compared with corresponding conventional fertilizer. Release of Phosphorous and Nitrogen were studied independently with a factorial experiment under four types of fertilizer in combination with three types of soils alfisol, inceptisol and vertisol. Cumulative Phosphorus and total mineral Nitrogen recovery significantly increased over conventional fertilizer. The increase in recovery was +88.3 % and +27.3 % for phosphorous and nitrogen respectively with nanomontmoillonite. Higher Recoveries were a result of slow release property of nanopolymers which reduced nutrient losses (Sarkar et al. 2014, 2015).

Nano-sized $AlZnFe_2O_4$/poly (Acrylamide-*co*-acrylic acid) superabsorbent nanocomposite was synthesized and the effects of different levels of nanocomposite were studied to evaluate the moisture retention properties of sandy loam soil. The soil amendment with 0.1, 0.2, 0.3 and 0.4 w/w% of nanocomposite enhanced the moisture retention significantly at field capacity compared to the untreated soil. Seed germination and seedling growth of wheat was found to be notably improved with the application of the nanocomposite. A delay in wilting of seedlings by 5–8 days was observed for nanocomposite-amended soil, thereby improving wheat plant growth and establishment (Shahid et al. 2012).

8.2.2 Nanominerals

Natural zeolites are hydrated aluminosilicates based on an infinite three-dimensional structure of tetrahedrons such as SiO_4, AlO_4, FeO_4 joined by oxygen atoms. Zeolites consist of interconnected channels and cavities of molecular dimensions where cations allowing the ion exchange exist. Zeolite materials allow an introduction of new functional groups through several processes of modification, improving substantially its activity and selectivity on the removal several substances (Inglezakis et al. 2002). Sulphate loaded nano zeolites were prepared and its activity was analysed in a percolation reactor (Thirunavakkarasu and Subramanian 2014). Sulphate release from fertilizer-loaded nanozeolite was available even after 912 h of continuous percolation, whereas sulphate from Ammonium sulphate was exhausted within 384 h.

The effectiveness of micro and nanoporous zeolite as a carrier for urea for slow release of nitrate was investigated by Manikandan and Subramanian (2014). Results revealed that the nitrogen release from the urea blended with nanozeolite (1:1) was up to 48 days while the conventional Zeolite – urea (1:1) mix was up to 34 day and the Nitrogen release ceased to exist in urea within 4 days without the presence of Zeolites.

Growth of Maize on sandy loam soil with and without the presence of porous silica nanoparticles was studied by Suriyaprabha et al. (2012).The increased surface area of silica nanoparticles led to accumulation of nanosilica in the plants and also increased the leaf size thereby leading to larger surface area for photosynthesis. Similarly, the effect of nano Si on growth characteristics of tomato was studied under salinity levels and has delivered promising results in salt tolerance (Haghighi et al. 2012). Using mesoporous silica as carrier for urea for slow release of nitrogen resulted in a fivefold increase in the availability period (Wanyika et al. 2012).

The supplement of the nanoscale hydroxyapatite was found to increase the level of chlorophyll and vitamin C and decrease the level of malondialdehyde in pakchoi plant shoots grown on Cd contaminated soil. The level of antioxidant enzymatic activity in the plant also increased as result of the addition of hydroxyapatite. The results confirmed that nanohydroxyapatite can be applied to reduce the plant uptake of Cd and resist the Cd stress (Li and Wu 2013). Nanohydroxyapatite was evaluated as a potential fertilizer to improve phosphorous availability in comparison with bulk hydroxyapatite and triplesuperphosphate for the growth of wheat (Montalvo et al. 2015). Although nanohydroxyapatite performed better than bulk hydroxyapatite, most likely because of faster dissolution, triplesuperphosphate was still a more efficient phosphorous fertilizer.

8.2.3 *Metal and Metal Oxide Nanoparticles*

Metal and Metal oxide nanoparticles such as Zinc, Iron, Titanium and their oxides have shown potential in promoting plant growth. Biosynthesized protein encapsulated, crystalline natured nano Zn (15–25 nm) was evaluated as a nanofertilizer for enhancing the growth of pearl millet. Beneficial effects were observed on shoot and root lengths, chlorophyll content leading to a grain yield of 37.7 % over the control without nano Zn (Tarafdar et al. 2014). Release of Zn to the soil using a nano-sized manganese hollow core shell was evaluated in a percolation reactor system. The results showed that the Zn-fortified core shell released Zn for more than 696 h while Zn release ceased after 408 h in $ZnSO_4$-fertilized soil (Yuvaraj and Subramanian 2014).

Beneficial effect of individual nano Fe, P and K on saffron flowering was analysed by Amirnia et al. (2014). Results indicated that nanofertilizers were effective in enhancing the flowering traits of saffron plant. Magnetite (Fe_3O_4) nanoparticles were synthesized and applied as foliar spray and soil additive to basil plant.

Nanoparticles applied were effective in increasing all the measured traits such as chlorophyll content, carbohydrate content, oil content shoot/root length etc. for both foliar spray and soil additive methods (Elfeky et al. 2013).

8.3 Soil Remediants

Anthropogenic activities have led to soil contamination is various parts of the world. Mining, agriculture, Industries, waste disposal are some of the factors which lead to soil pollution. An estimated 3,000,000 potentially contaminated sites are present globally which not only pose risk to human health, ecosystem but also pose a huge economic loss (Singh and Naidu 2012). Common contaminants include petroleum hydrocarbons, chlorinated solvents, persistent organic pollutants, pesticides, inorganics, heavy metals and radioactive constituents (Naidu 2013). Soil remediation methods are well established and have been in use for decades. Remediation technologies could be exsitu or insitu. Table 8.2 gives a summary of the remediation technologies available and the contaminant classes treated.

Nanomaterials with their enhanced reactivity towards contaminants and better mobility could be a potential choice for remediating soils. The application of nanomaterials for mitigating soil pollution includes degradation of pollutants, detection and sensing of pollutants, enhancers for remediation processes. Table 8.3 gives a summary of the research work carried out for evaluating the role of nanoparticles for soil remediation.

Table 8.2 Methods used for soil remediation and the contaminant classes

Method	Contaminant classes
Physical/chemical methods	
Soil vapor extraction	Halogenated and nonhalogenated organic compounds; inorganics; radionuclides; explosives
Stabilization	Halogenated and nonhalogenated organic compounds; hydrocarbons; explosives; inorganics
Chemical oxidation/reduction	Halogenated and nonhalogenated organic compounds; hydrocarbons; explosives; inorganics; radionuclides
Soil washing	Halogenated and nonhalogenated organic compounds; hydrocarbons; explosives; radionuclides
Electrokinetic seperation	Halogenated and nonhalogenated organic compounds; hydrocarbons; explosives; radionuclides; inorganics
Biological treatment	
Bioremediation	Organic compounds; inorganics; radionuclides
Bioventing	Organic compound; explosives; radionuclides; inorganics
Phytoremediation	Halogenated and nonhalogenated organic compound; hydrocarbons; explosives; Radionuclides; inorganics
Thermal treatment	Explosives; radionuclides; inorganics

Table 8.3 Nanoparticles used for soil remediation

Nanoparticles	Purpose	Degradation/ treatment method	Reference
Manganese peroxidase immobilized on nanoclay	Polyaromatics hydrocarbons	Transformation	Acevedo et al. (2010)
Apatite with carboxy methyl cellulose stabilizer	Lead	Immobilization	Liu and Zhao (2013)
Apatite	Atrazine	Dechlorination	Satapanajaru et al. (2008)
Hydroxyapatite	Lead	Immobilization and reduce lead accumulation in plants	Shaheen and Rinklebe (2015)
Hydroxyapatite	Cadmium/lead	Enhance phytoremediation	Wang et al. (2014)
Hydroxyapatite	Cadmium,	Adsorption	Chen et al. (2010)
	Zinc		
	Lead		
	Copper		
Nanosilicone	Lead	Stabilization	Liu et al. (2015)
Carbon black	Copper/zinc	Immobilization	Wang et al. (2009)
Surface modified carbon black	Copper/zinc	Immobilization	Cheng et al. (2014)
Nano Ca/CaO	Radioactive cesium	Ball milling for immobilization	Mallampati et al. (2012, 2013)
Nano zero valent iron	Triethylene	Enhancing phytoremediation by immobilizing triethylene	Martínez-Fernández et al. (2014), (2015)
	Chlorpyrifos	Degradation	Reddy et al. (2013)
	Lead polychlorinated biphenyls		Gao and Zhou (2014)
	Cr (VI)	Electrokinetics and PRB	Shariatmadari et al. (2009)
	DDT	Degradation	El-Temsah et al. (2013)
	Pyrene	Degradation	Chang et al. (2007); Chang and Kang (2009)
		Degradation	Alidokht et al. (2011)
		Degradation	Chrysochoou et al. (2012)
	Molinate	Electrokinetic	Gomes et al. (2014)
	Trichloroethylen	Permeable reactive barrier	Katsenovich and Miralles-Wilhelm (2009)
TiO_2/CeO_2	Cu	Reduce phytotoxicity	Wang et al. (2015)

(continued)

Table 8.3 (continued)

Nanoparticles	Purpose	Degradation/ treatment method	Reference
CMC stabilized nano Pd/Fe	Pentachlorophenil	Electrokinetic reduction	Yuan et al. (2012)
Nanomaghemite and magnetite	Cd, Cu, Pb	Stabilization	Michalkova et al. (2014)
CMC-Pd/nFeO	HCH (pesticides)	Degradation	Singh et al. (2012, 2013)
Nano Ca/CaO	Radioactive cesium	Immobilization by thermal treatment	Mallampati et al. (2015)
Nanomaghemite	Fe/Al/Mn	Immobilization/ phytostabilization	Vitkova et al. (2015)
Fe/Ca/Cao	Cesium	Grinding	Mallampati et al. (2015)
Pd/nFe	Polychrorinatedbiphenyls	Dechlorination	Le et al. (2015)
Nano Ca/CaO	Heavy metals		Mallampati et al. (2013a, b) and Mallampati et al. (2014)
Polyurethene	Phynethrene	Soil washing	Kim et al. (2003, 2004)
ZnO, Al	Heavy metals	Sorption	Mahdavi et al. (2015)
TiO_2	Pyrene	Photocatalytic	Chang et al. (2011)
	Phenanthrene	Photocatalytic	Gu et al. (2012)
MnO_2	Pyrene	Photooxidation	Chang et al. (2011a, b)

8.3.1 Nanomaterials for Contaminant Stabilization

Stabilization techniques effectively reduce the hazard potential of a contaminant by converting it into less soluble, mobile or toxic forms. Stabilization could be done either by physical methods or chemical reactions. The mobility of organic and inorganic compounds can be reduced through various precipitation, complexation, and adsorption reactions. The potential of Fe nano oxide (maghemite and magnetite) and amorphous Mn oxides for stabilizing Cd, Cu and Pb in contaminated soils was investigated by Michálková et al. (2014). Results from batch and column experiments coupled with adsorption tests proved that the amorphous MnO was the most effective treatment for the stabilization of metals in the studied soil samples at the given w/w ratios (1 and 2 %, w/w). Metal stabilization was a result of combined specific adsorption onto the oxide surface together with an increase in soil pH promoting the adsorption of metallic cations. Nano TiO_2 and CeO_2 were utilized to adsorb Cu(II) and mitigate its bioavailability and toxicity to Tobacco plants (Wang et al. 2015a, b). The addition of the nanoparticles along with humic acid resulted in increased the root length by 90 % and 100 % for nano TiO_2 and nano CeO_2 respectively. The results indicated that nanoparticles were successful in reducing the

Cu(II) phytoxicity by reducing the bioavailable soluble Cu(II). The study also reported no phytotooxicity by individual TiO_2 and CeO_2 nanoparticle which makes their usage more amenable.

The effect of nano zero valent iron (nZVI) coated with carboxy methyl cellulose on the degradation of DDT in soil columns was investigated by El-Temsah et al. (2013). Addition of nZVI and subsequent leaching with water led to a reduction in DDT concentrations in soil of almost 50 % compared to controls without nZVI. However the use of nZVI resulted in negative effects on plant growth. It was also observed that the oxidation of nZVI with aging reduces the negative effects of the presence of nanoparticles. Le et al. (2015) developed an integrated remediation system for dechlorination of aroclor 1248 using chemical catalysis and biodegradation. Dechlorination was achieved by treatment with bimetallic nanoparticles Pd/nFe under anoxic conditions. Dechlorination efficiency was 99 %, 92 %, 84 %, and 28 % of tri-, tetra-, penta-, and hexachlorinated biphenyls, respectively. The resulting biphenyl was found to be biodegraded rapidly by *Burkholderia xenovorans* LB400.

8.3.2 Nanomaterials in Thermal Treatment

Thermal treatments for soil remediation include incineration, steam injection and extraction and vitrification. Vitrification is a high temperature process in which organic matter is incinerated and mineral matter is melted and a slag is quickly cooled to obtain the contaminant entrapped in a matrix. Nano Ca/Cao mixtures were used to immobilized radionuclides ^{133} Cesium from contaminated soil through vitrification. The removal efficiency achieved with the nanoparticles was 96 % at 1,200 °C. The investigation results have showed that a certain amount of 133Cs was the entrapped inside new aggregates, produced during the thermal treatment with nCa/CaO (Mallampati et al. 2015a, b).

Thermal desorption of polychlorinated biphenyls in the presence of nZVI was evaluated by Liu et al. (2014). The presence of nZVI gave improved efficiency of desorption at 300 °C. The desorption efficiency was dependent on nZVI concentration and temperature. Nano Zerovalent Iron was also used to enhance thermal degradation of polychlorinated dibenzo-. p-dioxins and dibenzofurans at low temperatures (Lundin et al. 2013).

8.3.3 Nanomaterials for Enhancing Phytoremediation

Phytoremediation is a low cost and effective insitu remediation method for contaminated soil reclamation. Phytoremediation involves uptake, containment, degradation of contaminants by plants. Several reports are available in literature evaluating the effect of nanomaterials for enhancing phytoremediation Gao and Zhu 2014; Wang et al. 2014, 2015) . The effect of nanosilicon on lead toxicity, uptake and accumulation in rice varieties Yangdao 6 and Yu 44 grown on lead contaminated soil was analysed by Liu et al. (2015). The biomass increased by 3.35–11.8 % higher and lead concentration in shoots and grains was reduced by 27–54 % and 21–41 % respectively by adding nanosilicone to lead contaminated soil. The results indicate that nanosilicone was effective in preventing the lead transfer from rice roots to aboveground parts by complexation with lead.

E-waste contaminated soil containing Pb and polychlorobiphenyls was remediated by phytoextraction using Impatiens balsamina in the presence of three different nanozerovalent iron particles – free, vermiculite supported and activated carbon supported zerovalent iron. Free and vermiculite supported nanozero valent iron were found to increase accumulation of Pb in plants and activated carbon supported nano zero valent iron reduced the bioavailability of Pb (Gao and Zhou 2013, 2014).

8.3.4 Nanomaterials for Electrokinetic Remediation

Electrokinetic remediation is an emerging technology which involves application of a low-intensity, direct current through the soil to separate and extract contaminants from soil. The current is applied across electrode pairs that have been implanted in the ground on each side of the contaminated soil. During the process positively charged chemical species, such as metals, ammonium ions, and some organic compounds, move toward the cathode, and negatively charged chemicals, such as chloride, cyanide, fluoride, nitrate, and negatively-charged organic species, migrate toward the anode. Various additives such as surfactants can be added to enhance the remediation process. The combined effect of nanozerovalent iron and electrodialysis of polychlorinated biphenyls (PCB) was evaluated by Gomes et al. (2014a, b). H^+ generated near the anode in electrodialytic chamber solubilized the transition metal from soils which in turn aided in dechlorination of PCB to biphenyl compound (Gomes et al. 2014a, b). Yang and Chang (2011) evaluated the treatment efficiency of combining emulsified nano zerovalent iron and electrokinetic remediation for Trichloroethylene (TCE) on contaminated soil. Electro kinetic remediation enhanced transport of nanoparticles through the soil matrix from anode to cathode chamber. During the transport, hydrophobic TCE diffuses into nano zerovalent iron present in the inner aqueous region through emulsion and becomes dechlorinated.

8.4 Conclusion

Nanotechnology has the potential to provide solutions for better soil management through improving nutrient quality of soil and alleviating soil pollution. Although the efficacy of Nanomaterials as plant growth promoters and remediation agents has been proved, knowledge of the fate and effect of nanomaterials in soil has to be careful considered. Nanomaterials have been reportedly toxic to various organisms

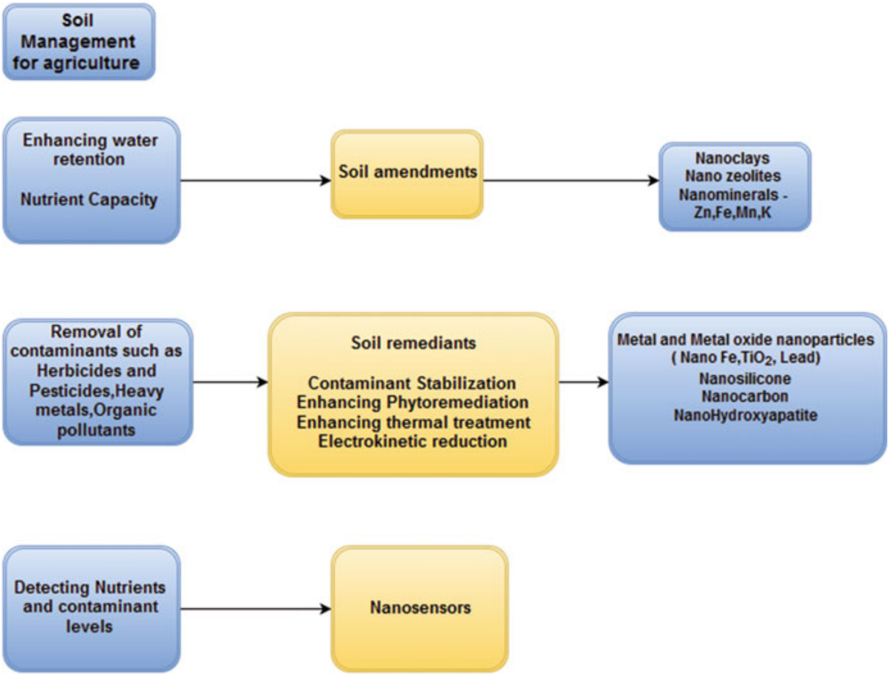

Fig. 8.2 Application of nanomaterials for soil management

and also effect human health (Mukherjee et al. 2014; Zou et al. 2014; Smulders et al. 2015). In this context, any new development involving the application of nanoparticles directly into the environment has to take into consideration the fate, transport and effect on the soil ecosystem, plant toxicity. Several researchers have attempted to understand the fate and transport of nanoparticles (Anjum et al. 2015; Sun et al. 2015) but many more investigations have to be carried out on the stability of the various types of nanoparticles alone and in combination with various contaminants (Fig. 8.2).

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Chapter 9
Nanofertilisers, Nanopesticides and Nanosensors in Agriculture

Hemraj Chhipa and Piyush Joshi

Abstract Nanotechnology has potentially promising applications to improve agriculture. Here we review the application of nanofertilizers, nanopesticides and nanosensors in agriculture. Nanofertilisers include Fe, Mn, Zn, Cu, Mo, Ti and carbon nanotubes. Nanofertilisers improve plant growth and save money because they are more efficient. Nanopesticides for plant protection include Ag, Cu, SiO_2 and Zn. Nanopesticides also save money because they are more efficient. Nanosensors are useful in precision agriculture, for instance to detect pests and weeds locally in real time, and thus to apply pesticides fast and locally. We also discuss toxicity and risk assessment of nanoparticles.

Keywords Agriculture • Nanotechnology • Nanofertilizer • Nanopesticide • Pest control • Nanotoxicity • Risk assessment

9.1 Introduction

Increasing global population is poignant on the yield of agricultural products and demanding innovations in global food security for fulfillment of daily need (Mura and Dudas 2013). The yield of agriculture is increasing, but the primary concern is safely and sustainable production. Previously, many applied technologies has been innovated in the agriculture sector for improvement of production such as, the usage of synthetic chemicals, genetically modified crops by biotechnology and evolution of pest resistant and hybrid varieties, but still a gap between the requirement and contentment of agriculture production looking for new technology (Zamir 2001; Zhu et al. 2000). The research and development give rise to several new technological innovations and the recent public figure in the limelight is nanotechnology (Mura and Dudas 2013; Appell and Jackson 2013; Handford et al. 2014).

Nanotechnology is a prominent technology in various fields such as electronic, electrical, optical, sensing, food and medical (Rai and Ingle 2012; Sozer and Kokini 2009). These tiny particles have specific physical, optical, chemical and mechanical

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characters which make them highly useful in comparative their bulk compounds. In the nanometer size range they are well composed which provides high volume to surface ratio for any application (Guo 2013).

Agriculture field is also looking towards this newly growing technology with great hope for future sustainability. The use of nanotechnology in agriculture is in the initial phase and need more research to provide a suitable solution for production improvement in sustainable manner (Lyons et al. 2011). It is hypothesized that nano-formulation/nanoparticles mediate delivery will provide site specific and controlled release of agriculture inputs e.g. fertilizer and pesticide, which will reduce the cost and the amount of agricultural input and make agriculture practices more productive through water and nutrient management (Bhattacharyya et al. 2010; Mukhopadhyay 2014). Reduction of chemical fertilizer and pesticide will be helpful in maintaining natural eco-balance of Geo-biological cycles, which have been destroyed or imbalanced by the use of synthetic chemicals (Alexander 1973). The continuous use of chemical in agriculture practices developed many disorders into growers and feeders and destroyed soil and water health also, making them toxic for the next generation. So the need of the time is to improve such drastic situation into a sustainable state of implementation of nanotechnology.

The use of metal nanoparticles, polymer based nano-formulation and encapsulation of fertilizers and pesticides is in nascent phase (Kashyap et al. 2015; Parisi et al. 2014). Many researchers have developed nano-formulation and encapsulation of agriculture inputs and applied on different agriculture crops in vitro and in vivo conditions. Kuzma et al. (2006) explained that nanotechnology can have different applications in agri-food sector such as food packing in the food industry, detoxification and nano-medication in animal husbandry, plant protection and fertilizer application, plant genetic modification, pollutant and water remediation in the environment and nano-sensing.

On the other side, as we know the negative impact of biotechnology in resistance development or genetic manipulation, similarly nanotechnology also has some adverse effect on biological and chemical environment (Sharma et al. 2004; Herdt 2006). So the environmental impact assessment is also necessary of nanotechnology before adopting in agricultural practices.

In the current article we reviewed the use of nanotechnology tools e.g. nanofertilizer, nano pesticide, nano sensor and nano herbicide in agriculture and their effect as growth promoters, nutrient supplement, pest controller and their environmental impact assessment. The advantage of nanotechnology in comparison to conventional farming practices is also summarized.

9.2 Need of Advancement in Agriculture

It had been centuries, since when the agricultural technology was continuously in developing approaches and thus has created huge changes in farmers live and contributed a lot in countries development, which can be clearly monitored through the countries per capita income. The expansion of towns and cities in the urbanized world has previously reinstate farmland with shopping malls, parking lots and housing developments. Thus, the needs of agriculture production uplifted and so increase the monetary value of crops and agricultural food items. Moreover, the major challenges faced by agricultural world include changing climate, sustainable use of natural resources and environmental issues like runoff and accumulation of pesticides and fertilizers. These troubles are further heightened by an alarm, increase in food demand that will be needed to feed an estimated population of 6–9 billion by 2050 (Chen and Yada 2011). Besides, it is widely acknowledged that global agricultural productivity must increase to feed a rapidly developing world population.

Today, there is increasing trend of Peri-urban agriculture and home gardening, which is becoming very significant in the developing world as a consequence of rapid urban growth. Therefore, new cultivar technology is required to fit into exhaustive construction systems, which may supply the food compulsory to fulfill urban world demands of the next century. The scientist is in the process to develop several new technologies for plants that are tolerated to urban pollution, proficient nutrient uptake and crop getting new substrates for growth. Also with the higher income, these clients may demand a more diverse diet. Food crops with low fats and high in specific amino acids may be needed to satisfy people who wish to change their eating habits (Naseer et al. 2014).

In modern agricultural systems farmers believe they own much more fundamental roles and are eager to use technology and information to control most parts of the agriculture system, a very different perspective from that of traditional farmers. In contrast to the isolation inherent in traditional systems, modern agriculture tends to ensure its success as dependent on linkages-access to resources, technology, management, investment, markets and supportive government policies.

As a result, much of the success of modern systems depends on the development and maintenance of soil fertility through the specific provision of nutrients when they are depleted, machine power and technology to make soil conditions to promote plant growth with minimal disturbance and minimal soil loss, the use of improved genetics for crops and livestock to enhance yields, quality and reliability and use of modern genetic and other techniques to protect plants and livestock from losses to competing plants diseases, drought insects and other threats.

Further, this could only become possible by adopting the latest technologies like biotechnology, which has been delivered specific agronomic trait development to overcome production constraints for perhaps 12 million of the world's farmers. This has resulted in improved productivity and profitability and has made important positive socioeconomic and environmental contributions even though only a limited range of agronomic traits have been commercialized so far for a small number of crops. The technology has delivered economic and environmental gains through a combination of their inherent technical advances and by facilitating the use of technology in more cost effective and environmentally friendly farming practices as suggested by Motes (2010) in its pre-publication draft.

Likewise, there are several profound structural changes occurred in the agricultural sector due to the fast development of technological innovations, but these also pose challenges such as sustainable production considering food security, poverty reduction and public health improvement. The agriculture and food production is of vital importance, as it has been one of the primary drivers of economy. The agricultural practices are often in the public eye because climate change, energy and resource constraints and rapidly growing global population are placing extraordinary pressure on food and water resources. By now scientific advances have touched all the facets in the field of agriculture. Thus we can witness a radical makeover for decades from handheld apparatus in the modern day Glass house/ Poly house, computer-controlled and GPS-monitored programs that virtually negate the need for human intervention. Moreover, attaining global food and nutrition security for 9.2 billion people by 2050 which means that food production will need to be increased by 70 % from current levels in a sustainable way while the environmental footprint of agriculture is reduced. Small field holder farmers in developing countries are expected to meet the food demand of emerging rural and urban regions. This demand is likely to increase to almost 90 % of total food demand by 2050 (Ghasemzadeh 2012). Traditional strategies like integrated pest management used in agriculture are insufficient nowadays and excess use of chemical pesticides like DDT has adversative effects on animals and human beings apart from the decline in soil fertility.

Consequently, If we talk about the current scenario in developing countries, where agriculture is considered as the backbone of the national economy, the countries are facing several serious issues such as lack of fertile agricultural soil, reduction of land due to competing infrastructural development activities, poverty and malnutrition, which need to be solved on a sustainable basis. The developing countries advancement in science and technology can offer potential solutions for discovering value addition in their current production systems. Therefore, these countries should enthusiastically contribute in research and development of these latest advance technologies, which have already greatly shown its impact on the agriculture industry. For example, earlier the farmers improved their crop production by inventing the first hoes, but today, they improve crop production through the use of global positioning systems. Nowadays, agricultural technology is also making inroads with the help of new but very promising fields of nanotechnology and genetic engineering. In past several scientific innovations also have led to the way of revolutionizing agriculture, which includes irrigation techniques, farm equipment, fertilization, and plant breeding. One of the most revolutionary agricultural innovations has been the development and use of biotechnology to increase crop protection and yield. Today, farmers in more than 30 countries around the world are planting seeds containing biotechnology traits. Seeds that utilize new breeding and biotechnology advances have helped these growers increase yields, reduce inputs and dramatically improve their profits (Fraley 2012).

Similarly, the results are expected from the flourishing applications of nanotechnology in agriculture, which will continue to rely on the problem-solving ability of the material and are unlikely to adhere very rigidly to the upper limit of 100 nm. This is because nanotechnology for agricultural applications will have to address the large-scale inherent imperfections and complexities of farm production systems (e.g. Use efficiency at extremely low input), that might require nanomaterials with flexible dimensions, which nevertheless perform tasks efficiently in agricultural production systems. This is in contrast with nanomaterials that might be working well in well-knit factory-based production systems (Mukhopadhyay 2014). With nano fertilizers emerging as alternatives to conventional fertilizers, build-up of nutrients in soils and thereby eliminating the chances of eutrophication and contamination of drinking water may be eliminated (DeRosa et al. 2010).

Moreover, the agricultural researchers and farmers worldwide will be facing the challenge during the next 25 years of developing and applying technology that can increase the global cereal yields by 50–75 %, and to do so in ways that are economically and environmentally sustainable is a great task.

Here the ray of hope lies in the application of nanotechnology in agriculture, which is astonishing till date. Research on the applications of nanotechnology in agriculture is less than a decade old. Nevertheless, as conventional farming practices become increasingly inadequate, and needs tremendous improvement, we have little option but to adopt and explore the latest technology such as nanotechnology in all sectors of agriculture.

Nanotechnology promises a breakthrough in improving our presently appalling nutrient use efficiency through nano-formulation of fertilizers, breaking yield and nutritional quality barriers through bio-nanotechnology, surveillance and control of pests and diseases, understanding the mechanism of host-parasite interactions at the molecular scale, development of new-generation fertilizers and pesticides. Moreover the nanotechnology applications in agriculture can be successful if natural processes are simulated in greater scientific sophistication/articulation for successful implementation.

9.3 Definition of Nanomaterial

The nano is defining the size of the matter in 10^{-9} m range. The Nanoparticles have the dimension of particles in the range of 1–100 nm. In this range each particle has specific mechanical, electrical and optical properties in comparison with their bulk matter which could be possible due to surface area per unit weight or volume increased enormously in the nano form. Due to their Surface Plasma Resonance (SPR), Enhanced Rayleigh Scattering and Surface Enhanced Raman Scattering (SERS) characteristics of nanoparticles have more advantage to bulk material and these properties make them the building blocks of optoelectronics, electronics and chemical and biochemical sensors of next generation (Gmucov 2012; Hahn et al. 2011; Gloskovskii et al. 2010).

Nanotechnology is viewed as "the next industrial revolution" by taking the advantages of these properties in order to develop new products (Lane 2002; Miley 2005). Nanotechnology has been explored in different applications due to their novel properties such as creating lighter and stronger material, ground water remediation, in substitution of harmful toxic chemicals in various applications, solar cell efficiency enhancement and as targeted drug delivery (Yan et al. 2012; Banik and Sharma 2011; Appell and Jackson 2013; Nakache et al. 2000). In this century the trend is toward miniaturization of the materials and nanotechnology is based on nano scale material with specific functionalities. The functionalization of the nanoparticles surface is one method for development of particle for specific application. Different shaped nanoparticles have been synthesized using different materials as spheres, nanotubes, nanohorns, nanoflowers and nanocages. The surface modifiers such as molecules, particles and polymers have different task, such as described by Guo (2013).

1. Stabilization of nanoparticles in solutions by controlling the growth at an embryonic stage and determine their shape
2. Provide functional groups on the surface
3. Increase solubility of nanoparticles in different solvents
4. Creating capping layer on the surface that modify physical and chemical properties of nanoparticle
5. Improve the assembling capacity of nanoparticles in specific array
6. Decrease the environmental toxicity of nanoparticles

The synthesis of nanomaterial for farming practices can be developed by top down and bottom-up method of understanding of the nano-dynamics of interacting nanomaterials and interfacing nanostructures. The synthesis of metallic nanoparticles has different routes of synthesis such as physical, chemical and biological but another type of nano-formulation using biopolymer, nano-capsulation and polymer-metal nano-composite also in developing stage (Fig. 9.1).

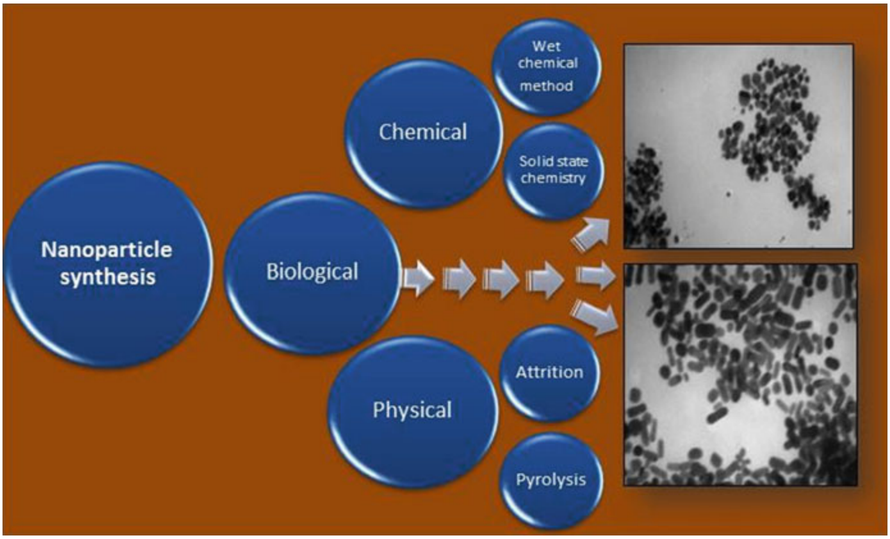

Fig. 9.1 Synthesis of nanomaterial using different routes including physical, chemical and biological. Chemical is based on solid and wet chemical method while, physical is mainly based on pyrolysis and attrition method and biological method is based on use of fungal, bacterial and plant extracts in reduction of bulk metal compounds

Physical method includes attrition and pyrolysis, while chemical method includes wet chemical and solid state interaction method. Physical and wet chemical methods are widely used in the synthesis of nanoparticles but these methods have some disadvantages. These procedures use enormous consumption of energy in order to maintain high pressure and temperature and uses of toxic solvents and generation of hazardous bi- products in chemical methods. So, cost effective, non-toxic and environmentally benign procedures for the synthesis of metallic nanoparticles are being used in the form of biological approaches (Thakkar et al. 2010).

In biological synthesis metallic nanoparticle has been synthesized by different species of bacteria such as Pseudomonas, Lactobacillus, Escherichia and Thermomonospora, different fungal strains such as Aspergillus, Fusarium, Phoma, Verticillium and different plant species as Alfa-Alfa, Aloe Vera, Azadirachta, Solanum and Lemon grass and algal strains such as Sargassum, Chlorella.

Fungi are the main biological matter, among bacteria, algae, virus and plants in the biosynthesis of nanoparticles due to their tolerance and bioaccumulation capacity of metal (Shankar et al. 2003). The fungus produces different type of extracellular enzymes, which is useful in large scale production of ecofriendly biomaterial, which provides economic viability and easy handling of the synthesis process (Jain et al. 2011).

9.4 Nanotechnology in Agriculture

Uncontrolled and longer time application of different conventional fertilizers would be dangerous for the agriculture sector and will raise environmental issue near future. It has been reported that heavy use of phosphorus and nitrogen fertilizer raising the eutrophication problem into surface water bodies world-wide (Conley et al. 2009), provide nutrition to phototrophic microorganism and help them into developments of algal bloom. Dubrovsky et al. (2010) reported that high use of manure and nitrogen fertilizer in agriculture zone increased the nitrate content, more than 83 % of shallow ground water zones in US have higher level of nitrate salt than maximum containment level (10 ppm) regulated by United state Environmental protection Agency (USEPA) in the United State.

Similarly, Rosenstock et al. (2014) reported that high nitrogen loading or uncontrolled use of fertilizer in agriculture accumulating the residues longer and their concentration increased rapidly in the ecosystem. In California nitrogen loading has increased from 81 to 163 kilo tonne per year within four decades (1971–2010). It is a serious concern about the continuous increasing residual concentration of fertilizer and pesticide in soil and water, which have crossed the limit and polluting environment. The conventional fertilizers have only 30–50 % efficiency. So, Researchers are looking for a sustainable solution to solve this critical condition, which is increasing with the time.

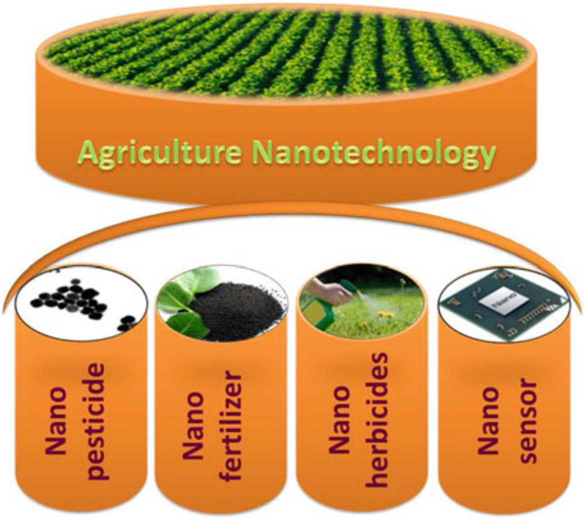

Fig. 9.2 Application of nanotechnology in agriculture: nanotechnology applies in the form of nano-fertilizer, nano-pesticide, nano-herbicide and nano-sensor for controlling nutrition, pest detection and management

Lal (2008) emphasized that nanotechnology could be a panacea for agriculture, like other sectors of development of a nano form of agriculture inputs e.g. nano-fertilizers and nano-pesticide, which have the greater capacity to provide site specific delivery of plant nutrients and improve the crop production in a sustainable manner. Similarly, many agricultural experts (DeRosa et al. 2010; Nair et al. 2010; Ghormade et al. 2011; Khot et al. 2012) interested in the development of nanotechnology based fertilizers. The output of nanoparticle application on plants at lab scale experiments developed a white hope for agriculture sector.

It is expected that nanotechnology covert conventional farming practices into precision farming practices. Chen and Yada (2011) concluded that “Precision farming is one of the most important techniques utilized for increasing crop productivity by monitoring environmental variables and applying targeted action”. So there is need to search a vital solution for sustainable agriculture development by innovating new agriculture inputs that provide high crop production, increase plant efficiency to nutrient use and reduce environmental destruction.

The nanotechnology will provide nano-supplement fortified feed and antimicrobial agents for animal production and nano-biosensor for diagnostic and precision farming practices. It would be possible that using nanotechnology, we can offer required quantity of nutrients and pest control agent to crop to maintain eco-balance and reduce excess runoff. In the form of nano-formulation, nano encapsulation and functionalized nanoparticles, this new technology provides lots of new opportunities in the development of new fertilizers, pesticides, herbicides, insecticide and sensor, which would have a capacity of controlled release and site specific delivery (Fig. 9.2).

The advantage of nano-formulation increases the solubility of poorly active ingredient by release of active ingredient in controlled manner and protection against premature degradation (Kah et al. 2013). Similarly, more advancement has been seen in pesticide sector, agrochemical companies also utilizing the advantage of nanotechnology by the development of chemical emulsion at nano-scale or nano-capsules contain active ingredients, which have the function of split open in response of the insect's alkaline condition or presence of heat and sunlight. Such advanced functionality of nano-pesticide will improve the efficiency and reduce the chemical dose and provide sustainable solutions for agro sector. Further, in the food sector, nanotechnology has the capability to solve many problems of food supply system. In the form of food polymers and polymer assemblage nanotechnology can contribute to the improvement of food safety and quality.

9.5 Use of Nano Tools in Sustainable Farming Practices

Nanotechnology is growing field of the current decade and it is widely applicable in the field of electronics, medicine, energy, automobiles, cosmetics, construction, food packing and paint industry. Likewise, agriculture is also touched by the use of nanotechnology in the form of nano-pesticide, nano-herbicide, nano-fertilizer and nano-sensor. The development of smart delivery system using nanomaterials has been open up new modes of novel applications in bringing the sustainability of the Agri-sector (Robinson and Morrison 2009; Joseph and Morrison 2006; Scott and Chen 2013).

9.5.1 Nanoparticles as Smart Delivery Agent

Nanotechnology could play a great role in sustainable agriculture practices by developing smart delivery system which is useful in environmental balance. Smart delivery system can provide a natural interaction between soil, plant and microbial communities of terrain. These advanced materials facilitate the nutrient management and control the nutrient transport such as Zn^{2+}, HPO_4^{2-}, $H_2PO_4^-$ and NH_4^+ in soil-plant system according demand.

Subsequently, nanoparticles are applying as smart delivery agent for fertilizers and pesticides in agriculture sector. These agriculture inputs are used with polymers, encapsulation or metal surface (ionic or weak bond) attachment. These smart delivery agents improve the stability and reduced the amount of product needed to be distributed. So excess chemical runoff can reduce and maintain the environmental balance. The nano-formulation of 100–250 nm sized nanoparticles has been attracting in agriculture by increasing the stability, ability to dissolve in water and increase activity. Similarly, nano-emulsion of 200–400 nm sized nanoparticles with pesticides and herbicide also attracting agriculture sector by enhancing their integration properties in different distribution medium (Solanki et al. 2015; Liu and Lal 2015). Further, nano-capsules are also an attractive tool of delivery in agriculture and the pharmaceutical industry. Nano-capsules are organic polymer or micelles based

Table 9.1 Recent breakthroughs of nanotechnology in agriculture sector; different type of products have been developed for agricultural applications by nanotechnology

S.No.	Product	Application
1.	Agricultural waste	Nano-fibers from cotton waste for improved strength of clothing
2.	Buckyball fertilizer	Ammonia from buckyballs
3.	Food packing	Airtight plastic packing with silica nanoparticle
4.	Nanocides	Nano-pesticide encapsulate in nanoparticle for controlled release
		Nano-emulsion for greater efficiency
5.	Nano-sensor	Pathogen detection, toxin detection, pesticide residue detection
6.	Precision Framing	Nano-sensor linked to soil condition and crop growth

Sastry et al. (2007)

nanostructure, which has the one lipophilic and other polar side. They contain the active ingredient inside the shell and release in the response of physiological change (Ali et al. 2011).

In contrast, such nanomaterials as zero valent iron or nanoparticle from iron rust have been used for remediation of soil, contaminated by heavy metals and pesticides. Iron nanomaterials also take part in soil aggregation and improve the soil binding capacity.

In the form of nano-formulation, these nanomaterials improve the nutrient efficiency of nano fertilizer by higher surface area. Similarly, nanomaterials are highly applicable in surveillance and pest and disease control, understanding of host-parasite interactions at the molecular level (Mukhopadhyay 2014). Some of the uses of nanotechnology in agriculture are listed in Table 9.1.

For enhancement of global agriculture production, one of the nano technological tools in the form of "nanofertilizer" is the potential tool which could helpful in fulfillment of the demand of a growing population by increasing the crop production. According to Liu and Lal (2015) nano-fertilizers are nanomaterials (NMs) which can supply one or more nutrients to the plants and enhance their growth and yields, which facilitate the improvement in the performance of conventional fertilizers. Primarily nano-fertilizers are divided into two categories based on plant nutrient requirement.

9.5.1.1 Macronutrient Nanofertilizers

In this category different macronutrient are included such as Nitrogen (N), Phosphorus (P), Potassium (K), Magnesium (Mg), Sulfur (S) and Calcium (Ca) which are essential for plant growth. In the conventional farming practices those macronutrients are heavily used on the farm and large amount of unused chemicals transported into ground water and surface water bodies, which increasing the threat to human health and aquatic life by disturbing the ecosystem balance. Therefore, development and innovation of nanofertilizer in the field of macronutrient supply in an ecofriendly and sustainable manner are much needed. Many researchers are working on the development of environmental friendly nanomaterial which can ensure the protection of environment and high crop yield. There are a few examples for instance, Liu and Lal (2014) developed a Ca and P based nanoparticles in the form of hydroxyapatite ($Ca_5\ (PO_4)\ _3OH$) and applied on Glycine max (Soybean) in greenhouse experiment and recorded 20 % and 33 % increment in seed yield and growth rate in comparison of regular phosphorus fertilizer. Similarly, Liu et al. (2004) reported that when 20–80 nm sized Ca NP in the form of $CaCO_3$ was applied at 160 ppm concentration on *Arachis hypogaea* (peanut), seedling growth was observed significantly. The total 15 % increase was measured in dry biomass in comparison to control. Magnesium (Mg) and iron (Fe) nanoparticles were used on *Vigna unguiculata* (Black eyed pea) by the foliar method (Delfani et al. 2014). In the seed weight of black eyed pea increased by 7 % when measured in comparison to bulk Fe and Mg salt and without Fe and Mn nanoparticle growing plants. Delfani et al. (2014) concluded that Fe and Mn nanoparticle could helpful in the improvement of photosynthetic efficiency.

9.5.1.2 Micronutrient Nanofertilizers

Micronutrients are the trace elements which are required to plant in minute quantity for different metabolic activities. There are different elements included such as iron (Fe), magnesium (Mn), Zinc (Zn), Copper (Cu), Molybdenum (Mo), Nickel (Ni), Boron (B) and Chlorine (Cl) as micronutrient (Table 9.2). Generally, these micronutrients are added with the macronutrients in the concentration of 5 ppm in composite fertilizers (Jones et al. 2012).

Iron Nanoparticles

Fe is the most important metal for plant growth, base of chlorophyll development and helped as a carrier of important elements circulation as blood stream. Researchers have been focusing on the development of such nanoparticles and their adaptability in agriculture worldwide. Ghafariyan et al. (2013) used Fe nanoparticle in the greenhouse experiment on Glycine max (Soybean) and observed that chlorophyll was increased in leaves significantly. They suggested that Fe nanoparticle could be used as iron supplement for soybean, which may helpful in preventing chlorotic symptoms of leaves. Similarly Delfani et al. (2014) reported that numbers of pods were increased in black eyed pea plant on the use of foliar spray of Fe nanoparticle at 500 ppm and Fe content was increased up to 34 % and chlorophyll up to 10 % in leaves in comparison to control.

Table 9.2 Effect of micronutrients on agricultural crop: different types of micronutrients have been developed in nano form and their effect on plant growth and physiology is summarized below

S.No	Nanoparticle	Crop	Concentration	Effect	References
1.	FeO	Soybean	30–60 ppm	Chlorophyll increased	Ghafariyan et al. (2013)
		Pea	250–500 ppm	Seed weight and chlorophyll increased	Delfani et al. (2014)
2.	Mn	Mung Bean	0.05–1 ppm	Shoot length, chlorophyll content and the photosynthesis rate increased	Pradhan et al. (2013)
3.	ZnO	Mung Bean and Chick Pea	1–2000 ppm	Plant growth increased at 20 ppm in mung bean and in check pea at 1 ppm	Mahajan et al. (2011)
		Cucumber	400–800 ppm in soil	Root dry weight and fruit gluten increased	Mahajan et al. (2011)
		Rap seed	1–2000 ppm	Root elongation	Lin and Xing (2007)
4.	Zn	Rye grass	1–2000 ppm	Root elongation	Lin and Xing (2008)
5.	CuO	Edodea Densa planch	0.023–5 ppm	Photosynthetic rate increased	Nekrasova et al. (2011)
6.	Cu	Lettuce seed	130–600 ppm	Shoot and root length increased	Shah and Belozerova 2009
7.	Mo	Chick Pea	8 ppm	Plant mass and number of modules increased	Taran et al. (2014)

Manganese Nanoparticles

Manganese (Mn) is the component of superoxide dismutase enzyme and is required at water splitting step in photosynthesis. Pradhan et al. (2013) used, Mnnanoparticle on *Vigna radiata* (Mung bean) and observed enhancement in growth and an increase in photosynthesis. They measured a 52 % increase in root length, 38 % shoot length, 71 % in the number of rootlets, 38 % in fresh biomass and 100 % increase in dry biomass at very low (0.05 ppm) concentration of Mn nanoparticle and suggested that Mn nanoparticle could be a better alternative of Mn micronutrient in comparison to bulk $MnSO_4$.

Zinc Nanoparticles

Zinc is the essential component of different enzymes such as RNA polymerase, alcohol dehydrogenase, carbonic anhydrase and superoxide dismutase and it is an essential element for chlorophyll biosynthesis in plant. Mahajan et al. (2011) applied

ZnO nanoparticle on *Vigna radiata* and *Cicer ariatium* (chickpea) seedlings at different concentration. They observed that ZnO nanoparticle at 20 ppm showed growth in term of root enhancement up to 42 % and 41 % in biomass, similarly in shoot length enhancement up to 98 % in comparison to control. In the case of chickpea at 1 ppm concentration root length was increased up to 53 % and shoot length up to 6 %. ZnO nanoparticle was also shown growth enhancement in *Cucumis sativus* (Cucumber) at 400–800 mg Kg^{-1} concentration in soil (Zhao et al. 2013a). Similarly, Lin and Xing (2007) applied ZnO nanoparticle on *Raphanus sativus* (Radish) and *Brassica napus* (Rape) and reported enhancement in root at 2 ppm. Subsequently, Raliya and Tarafdar (2013) used biosynthesized nanoparticles on cluster bean and measured significant improvement in plant growth at 10 ppm concentration. They reported that in the presence of ZnO nanoparticle cluster bean showed 27.1 % increment in biomass, 31.5 % in shoot length, 66.3 % in root length, 73.5 % in the root area, 276.25 in chlorophyll, 27.1 % insoluble protein and 73.5 % in phosphatase enzyme activity.

On the other hand, toxic or inhibitory effect of ZnO nanoparticle also assessed at higher concentration (400 to 2000 ppm) by many researchers (Lee et al. 2010; Lin and Xing 2007; López-Moreno et al. 2010; Zhao et al. 2013b).

Copper Nanoparticles

Copper is also a component of many plant enzymes and essential for plant growth. Nekrasova et al. (2011) reported that at low concentration (0.25 ppm) Cu nanoparticle improved the photosynthesis by 35 % in *Elodea densaplanch* (waterweed). As same Shah and Belozerova (2009) also reported improvement in seedling growth of lettuce by 40 % at 130 mg Kg^{-1} of Cu nanoparticle in soil. In contrast, at 200 to 1000 ppm Cu nanoparticle showed toxic effects on mung bean, *Triticum aestivum* (Wheat) and *Cucurbita pepo* (Yellow Squash) (Lee et al. 2008; Musante and White 2012; Stampoulis et al. 2009).

Molybdenum Nanoparticles

Molybdenum (Mo) nanoparticle is an important element of nitrogen fixation system in plants. Many scientists have been working on development of Mo nanoparticle. In this context Taran et al. (2014) reported that Mo nanoparticle with nitrogen fixing bacteria treatment to chickpea seed showed enhanced growth two to three times in comparison to water, only Mo nanoparticle, only nitrogen fixing bacterial incubation treatment and concluded that this combination could be the optimal treatment for better plant nutrition and Mo nanoparticle increases the microbial activity. Another type of nanoparticle such as TiO_2, SiO_2 and CNT also used as growth promoters in plants except micro and macro nutrients.

TiO_2 Nanoparticles

Titanium oxide nanoparticle also showed good agreement with plant enzyme activity, enhance plant growth. On the exposure of sunlight, it improves the photosynthesis activity and helpful in chemical nitrogen fixation in the air. Lu et al. (2001) reported that TiO_2 and SiO_2 nanoparticle mixture accelerate germination and growth of *Glycine max* (soybean) by increased nitrogen fixation by enhancing the activity of nitrate reductase in the rhizosphere. Gao et al. (2006) used TiO_2 nanoparticle in seed treatment and foliar spray in *Spinacia oleracea* (Spinach). They first socked the spinach seeds in TiO_2 nanoparticle solution at 250 ppm for 48 h under light and after germination of seedlings sprayed TiO_2 nanoparticle solution once a week for 35 days in green house experiment. They reported that use of TiO_2 nanoparticle increased the total nitrogen, chlorophyll and protein content by 23 %, 34 % and 13 %, respectively, weight of the plant also increases two times in comparison to control. Further, Gao et al. (2006) and Song et al. (2013) showed growth enhancement only at low concentration, higher than 50 ppm.

Carbon Nanotubes

Carbon nanotubes (CNT) also applied as growth promoter in different plant systems (tomato, soybean, cabbage, carrot, rye-grass, rape and corn) and showed a positive and negative impact on plant growth at different concentrations. Lin and Xing (2007) used multi walled carbon nanotubes on rye-grass, rape and corn and reported enhancement in root elongation of germinated seed at 200 ppm. Similarly, Cañas et al. (2008) also reported incensement in root length of *Allium cepa* and cucumber seed at an exposure of single walled carbon nanotubes at different concentration. In the other hand, no positive result was measured on cucumber, radish and lettuce seed. carbon nanotubes also showed positive impact on production of crops by effected water channel protein expression through surface charges of carbon nanotubes in a tomato plant, which increase the water uptake capacity and utilization efficiency (Villagarcia et al. 2012). Subsequently, Khodakovskaya et al. (2012) reported that carbon nanotubes increased the tomato production by twofold at 50 ppm concentration in comparison to control. Srinivasan and Saraswathi (2010) applied carbon nanotubes on tomato and explained that carbon nanotubes facilitate water uptake capacity and plant growth by entering into germinating tomato seeds.

9.5.2 *Dynamics of Nanofertilizer*

In the recent review by Liu and Lal (2015) described the thermo dynamical concept of nanofertilizer penetration inside the plant cell. They proposed that the entropy of a single particle is based on randomness and in emulsion form, nano colloids have more suspension compared to ordinary fertilizer grade due to high entropy. Entropy is directly proportional to Gibbs free energy. Movement of particle depend on Gibbs free (G) energy and increase in Gibbs energy of colloidal particles will increase their movement which increases the permeability of colloidal particles across the semi-permeable membrane and after penetration nanoparticle enter inside the xylem.

According to rule of thermo dynamics G = H-TS (G = Gibbs Free energy; H = Enthalpy; S = entropy and T = Temperature) If Gibbs energy is negative, the reaction is spontaneous and moves in a forward direction. If Gibbs energy is zero, the reaction is at equilibrium and if Gibbs energy is positive, then the reaction is non-spontaneous. Nanoparticles enter into the plant through binding with carrier proteins and transfer by aquaporin, endocytosis, ion channels and pores (Rico et al. 2011).

9.5.3 Nanoporous Nanomaterial

Nano-porous nanomaterial provides a new advantage of carrier nanoparticles. They have uniform pore size, well established pore channels, high surface area and special liquid permeability, which provide benefits to agriculture and food sector (Dai and Ju 2012). The pore size of mesoporous material contains between 2 and 50 nm, while in macro-porous material it is approx 50–1000 nm and in micro-porous material they possess from 0.2 to 2 nm (Ravikovitch and Neimark 2001). Nano-porous material is applicable in the detection of pathogen, detection of toxin, catalyst and controlled release material for pesticide and fertilizer delivery. These nanomaterials have control on delivery of bioactive compounds to target points in needed amount. Functionalization of such material provides additional feature in the form of tuning of release rate. Use of these materials in agriculture fields reduces the quantity of fertilizers and improves efficiency. Further, Zhang et al. (2011) reported that nano-porous material, pore size, wall thickness and structure significantly influence the release rate. They investigated the ability of nano-porous silica to release menthol and describe that functionalization of surface with hydrophobic groups reduce the release rate of menthol by nano-porous silica in aqueous solution. Subsequently, Yan et al. (2012) also explained that the release rate of nano-porous material depends on external factors such as ionic strength, pH and salt concentration in the medium. They worked on multilayer microcapsule of poly (L-glutamic acid) /Chitosan and investigate the release rate of 5-fluorouracil compound in different conditions. They reported that pH and salt concentration also affected the loading capacity of the drug in nano-porous capsules and acidic condition promotes the continuous release of the drug.

9.5.4 Nanosensors

Nanotechnology has more promising application in the field of agriculture in the form of nanosensor. Nanosensors provides real time information about detection or location of the pathogen, pesticides and beneficial in prediction of environmental condition, field condition and real time monitoring of the crop (Chen and Yada 2011). Such information would be useful in protecting the crop from pathogens, pests, viruses, weeds and improve production by proving suitable nutrients to the soil. These sensing systems make the conventional agriculture system into precision farming practices. Yao et al. (2009) synthesized fluorescent nano-probes of silica nanoparticles conjugated with goat anti rabbit secondary antibody for detection of plant pathogen *Xanthomonas axonopdis*, which produce bacterial spot disease in Solanaceous plants. Further, in these probes Yao et al. (2009) use Tris-2, 2′-bipyridyl dichloro ruthenium hexa hydrate dye on to the core surface of silica nanoparticles which produce fluorescence. Carbon nanoparticles are also used in nanosensor development. Sharon and Sharon (2008) developed carbon nanomaterial based chemical sensor for detection of pesticide residue in plants.

9.5.5 Role of Nanotechnology in Plant Protection and Pest Management

In current decade nanotechnology is getting more attention in controlling pest and diseases of crops plants. Nano-formulation with metal nanoparticles or polymer based formulation of pesticides is in demand in the pesticide research field. Nanoparticle has been used for DNA and chemical delivery into plant tissue for protection from pathogens showing promising application of nanotechnology in nanoparticle mediate gene transfer (Torney et al. 2007). Another form of the nano tool as nano-encapsulation of pesticide is known for controlled and slow release of the active compound by manipulation of the outer shell of the capsule, which promotes the release of pesticide with low dosage over a prolong period and prevent unwanted pesticide runoff in the environment (Agrawal and Rathore 2014; Khot et al. 2012).

Similarly, Nair et al. (2010) concluded that these nano carriers have the ability to provide controlled and site targeted delivery of Agrochemicals in the plants. The synthesis of such nanomaterial is based on polymer encapsulation with lipid, viral capsid and clay have ecofriendly and biodegradable material which release the agrochemicals under structural manipulation. Nano-capsule and nanoparticles have the size in the range of 0.1–1000 nm is most relevant in plant protection. The nano – capsule has the shell which contains bioactive compounds in his core. This nanocapsule are helpful in penetration of agrochemicals in plant tissue, provides stability to active compounds and release slowly, gradually or completely after the shell opening. Shell opening is based on the outer circumstance of nano-capsules and depends on the change in physiological pH or enzymatic degradation. Additionally, Wang et al. (2007) synthesized nano-emulsion of pesticide using oil and water used against different insect pest and found effective to control pests. Further, solid-lipid nanoparticles loaded with essential oil also used for nano-pesticide formulation (Liu et al. 2006). Subsequently, Pérez-de-Luque and Rubiales (2009) reported that nano encapsulated herbicide reduced the eco-toxicity of herbicide against parasitic weed. Nano-silica is also used to control different insect pests (Rahman et al. 2009). The advantage of nanocapsule in agriculture application is given below

1. Absence or less of phytotoxicity
2. Reduction of harmful residues in soils
3. Reduction of chemical compounds uses for nutrition and protection of crops
4. High selectivity towards the crops treated
5. High quality and no harmful residues in the final products
6. Low production costs

Recently different type of nanoparticles used in pest management and further research is going on for their efficiency improvement (Table 9.3). Description of some nano pesticides is given below.

9.5.5.1 Silver Nanoparticles

Silver is a highly known antimicrobial metal in ionic and nanoparticle forms since long back. Kim et al. (2007) reported that silver kills the unicellular microorganism by inactive their enzyme system. Silver is also reported as a plant growth promoter (Kumar et al. 2010). Silver nanoparticles are reported as controlling agent against different plant pathogen such as *Fusarium culmorum*, *Rhizoctonia solani*, *Scalerotinia sclerotiorum*, *Biploaris sorokiniana, Colletotrichum gloeosporioides, Magnaporthe grisea, Phythium ultimum Botrytis cinerea, Phoma* and *Magnaporthe grisea* (Gopal et al. 2011; Park 2006; Gajbhiye et al. 2009). Further, Park et al. (2006) demonstrated spray of silica–silver nanoparticles on powdery mildew infected leaves of pumpkin and observed silica-silver alloy prevented powdery mildew disease of pumpkin within 3 days of spraying. Similar, Kumar et al. (2010) studied the antifungal effect of silver nano colloids against powdery mildew pathogen of rose (*Sphaerotheca pannosa*). Likewise, Kim et al. (2007) synthesized three types of Ag nanoparticle and used as an antifungal agent against *Raffaelea sp.*, a pathogenic fungus of oak tree in Korea. They observed that Ag nanoparticle showed detrimental effects on fungal mycelia as well as on conidial germination. Jo et al. (2009) tested Ag nanoparticle on fungal pathogens of spot blotch of wheat (*Bipolaris sorokiniana*) and rice blast (*Magnaporthe grisea*) and reported that comparatively *M. grisea* showed more inhibition to silver nanoparticles. In another study on *Lolium perenne* (rye-grass) showed significant reduction by silver ions and nanoparticle. Gajbhiye et al. (2009)) investigated the effect of biological synthesized silver nanoparticle and observed enhancement in antifungal activity of trizole against *Phoma glomerata, Trichoderma* sp. and *Candida albicans*.

Table 9.3 Use of nanomaterials as pathogens control agent: different types of nano-pesticides showed significant impact in pest control. The effect of these nano-pesticides are summarized in the table

S.No.	Nanomaterial	Application	Act against	Effect	Reference
1.	Nano silver	Antibacterial activity of nano-silver towards the control of cabbage black rot	*Xanthomonas campestris pv. campestris*	Significant reduction of cabbage, black rot in the pot experiment	Gan et al. (2010)
2.	Validamycin loaded nano sized calcium carbonate	Controlled release of validamycin loaded nano sized calcium carbonate (50–200 nm)	*Rhizoctonia solani*	Better germicidal efficacy and slow releases of nano formulation of validamycin upto 2 weeks	Qian et al. (2011)
3.	Thiamine di-lauryl sulfate (TDS) nano particles	Antifungal activity of TDS nano-particles (258.6 nm) against fungus associated with pepper anthracnose	*C. gloeosporioides*	80 % growth inhibition *of C. gloeosporioides* and TDS nano particles showed destruction of the Haifa	Seo et al. (2011)
4.	Chitosan nano particles (CSNPs)	Efficacy of CSNPs on fungal growth and chili seed quality	*Rhizopus sp. Colletotrichum capsici, C. gloeosporioides, and Aspergillus Niger*	Delayed mycelia growth in comparison to control	Chookhongkha et al. (2012)
5.	Nano copper	Antibacterial activity, the causative of pomegranate bacterial blight	*Xanthomonas axonopodis pv. punicae*	Nano copper inhibited the growth >10,000 times efficiently than that usually recommended dose of Cu-oxychloride	Mondal and Mani (2012)
6.	Light activated nanoscale formulations of TiO2	Nanoscale formulations of TiO2 with Ag and Zn on towards the control of bacterial spot of tomato	*Xanthomonas perforans*	High photocatalytic activity as compared to control and the significantly reduced bacterial spot without causing any adverse effects on yield	Paret et al. (2013)

7.	Copper nano particles	Cu-based NPs (11–55 nm) were tested on tomato (*Lycopersicon esculentum*) work for their antifungal activity	*Phytophthora infestans*	More effective than the commercial Agrochemicals at lower concentrations and drastically reduced the active ingredient rate	Giannousi et al. (2013)
8.	DNA directed silver nano particles on graphene oxide	Antibacterial activity of nano particles	*Xanthomonas performance*	Reduced the bacterial spot disease compared to untreated tomato transplants	Ocsoy et al. (2013)
9.	Light-activated nano particle formulation of Titanium dioxide with zinc	Nano composite for management of bacterial leaf spot on Rosa ‘Noare’	Bacteria	Significantly reduced bacterial spot compared with the untreated control and other commercial bactericides	Paret et al. (2013)
10.	Chitosan based nanoparticles (Chitosan, Chitosan- saponin and Cu-Chitosan nanoparticles)	In vitro evaluation of Chitosan based nano particles	*Alternaria alternata, Macrophomina phaseolina* and *Rhizoctonia solani*	Most effective in inhibiting spore germination and showed 89.5 %, 63.0 % and 60.1 % growth inhibition of *A. alternata, M. phaseolina and R. solani* respectively	Saharan et al. (2013)

Chowdappa and Gowda (2013)

9.5.5.2 Copper Nanoparticles

Cu nanoparticle is also reported effective against disease spread by *Xanthomanas* sp. such as rice bacterial blight disease (*Xanthomonas oryzae*) and leaf spot of mung by *Xanthomonas campestris*. Esteban-Tejeda et al. (2009) reported that Cu nanoparticles have broad spectrum antimicrobial activity against Gram positive and negative bacteria and fungi, at low concentration it can be used as a fungicide (Giannousi et al. 2014). Similarly, Cioffi et al. (2005) measured antifungal activity of nano-composite of copper with polymer against plant pathogens.

9.5.5.3 Silica Nanoparticles

Silica is recognized as a vital element in plant physiological activities and growth inducer (Kanto et al. 2004) which would helpful in proliferation of the stress resistance capability of diseased plants (Brecht et al. 2004). Silica nanoparticles have reported effective in control of insects like *Trialeuroded vaporarium* (white fly), *Dermanyssus gallinae* (Coconut mite*), Phaedon weevil* (mustard weevil), *Sitophilus oryzae* (rice weevil). There has been no report of silica nanoparticle as antimicrobial agent, but in combination with Ag (Ag-Si) nanoparticle showed anti-bacterial and anti-fungal activity (Park et al. 2006). They reported at 10 ppm concentration Si-Ag nanoparticle showed 100 % inhibition of fungal growth while in the case of bacterial concentration was 100 ppm. Further, Si-Ag nanoparticles showed 100 % control of powdery mildew disease in cucurbits and these nanoparticles showed phyto-toxicity at 3200 ppm concentration in cucumber and pansy plant (Park et al. 2006). In another form, silica is highly applicable in transformation (targeted delivery of DNA and gene of interest) and chemicals through its mesoporous structure (Wang et al. 2002). In mesoporous form nanoparticle have well organized pores which increase their surface. Liu et al. (2006) also reported that pesticide validamycine loaded into porous hollow silica nanoparticle (PHSN) can be efficient delivery system. These PHSN can provide controlled delivery of pesticide according to need of the plant. Barik et al. (2008) used nano-silica as a pesticide against insect and reported that nano-silica absorbed into the cuticle lipid of insects by physio-sorption and kill insects.

9.5.5.4 Zinc Nanoparticles

Zinc nanoparticles has been used as nanofertilizer on many crops and its showed positive results in optimal concentration, but the ZnO as fungicidal against fungal plant pathogen is less studied. He et al. (2011) applied ZnO nanoparticle against fruit mold *Penicillium expansum* and *Botrytis cinerea* and measured significant reduction in growth of pathogen. Similarly, growth reduction was observed against *Aspergillus flavus* and *Aspergillus niger* by Jayaseelan et al. (2012).

Table 9.4 Application of nano-formulations as carrier and pest controlling agent for crop protection; use of different base materials in formation of nano capsules are summarized below

Type of nano capsule	Delivery of compound	Application	Reference
Vernonia oil	2,4 D	Delivery through plant Barrier	Wiesman et al. (2007)
Lipid nano disc	Amphotericin B	Delivery in plants	Pérez-de-Luque and Hermosín (2013)
Chitosan	Pesticide	Delivery in plants	Ding et al. (2011), Feng and Zhang (2011), and ad Yin and Zhang (2010)
Alginate-chitosan	Paraquat	Transport of herbicide	Dos Santos Silva et al. (2011)
Starch	Plant oil	Encapsulation of plant oil	Glenn et al. (2010)
Cyclodextin complex		Soil amendment for decreasing herbicide photo-degradation	Morillo et al. (2001)
Poly (hydroxybutyrate-co-hydroxyvalerate	Atrazine and ametryn	Controlled release of herbicides	Grillo et al. (2010) and (2011)
Ethylcellulose	Nonflurazon and alachor	Controlled release	Sopeña et al. (2005, 2007)
Virus	Viral protein	Bio insecticide	Summers (2006)

Pérez-de-Luque and Hermosín (2013)

ZnO nanoparticle showed less toxicity in comparison to Ag nanoparticle to the plant and can be applicable as nano pesticide.

In the same context, nano-sulfur and nano formulation of conventional pesticide (hexaconzole) also used against plant fungal pathogens. Plant fungal pathogen *Rhizoctonia solani* and *Erysiphe cichoracearum* could be controlled by use of nano-formulation of hexaconzole and nano sulfur. Nano sulfur is also active in controlling red spider mite (*Tetranychus urticae*) which is ten times more effective as compared to commercial sulfur. In the other study, Yang et al. (2009) used PEG coated nanoparticles loaded with essential oil of garlic against *Tribolium castaneum* insect and observed 80 % control of insect based on slow and continuous release of essential oil of garlic from nanoparticles.

In the recent review by Rai and Ingle (2012) described the use of nanotechnology in pest management (Table 9.4). Many researchers used different type of nanoparticle to control the insect pest. Comparative study on the effectiveness of different type of nanoparticles such as AgNP, ZnO, TiO_2, and aluminium oxide nanoparticle against rice weevil, *Sitophilus oryzae* and baculovirus were done by Goswami et al. (2010). They measured that aluminium nanoparticle showed 100 % mortality while Ag NP showed 95 % mortality after 7 days. Similarly, Stadler et al. (2010) showed insecticidal activity of nano alumina against *Rhyzopertha dominica* and

S. oryzae and reported that nano alumina is the reliable and cheap alternative of commercial insecticides.

A lot of product has been come into market for different applications, but the impact of these nanoparticles in the environment should be monitored. Further, the regulation for product registration by Federal insecticide, fungicide and rodenticide, Act of Nano-pesticide is required so the product will not generally cause unreasonable adverse effect on the environment. All nanotechnology based products should complacence with Toxic substance control act (TSCA). TSCA is the act which regulates the chemicals by providing a regulatory framework for chemical production, use and their disposal method. It applies to any persons which has the relation to manufacturing, processes and distribution of chemical substance at commercial level.

9.6 Nanotechnology Versus Conventional Practices

As compared to the conventional practices the use of nanotechnology can play an important role in improving agricultural productivity by decreasing agricultural consumption of water and decreasing environmental pollution caused by agricultural runoff. If we talk about the role of nanotechnology in modern agriculture system, it can be considered as one of the most significant tools and can be predicted to become a driving economic force in the near future. Nanotechnology has a tremendous potential to revolutionize agriculture and allied fields, including aquaculture and fisheries. Nano agriculture focuses currently on target farming that involves the use of nano sized particles with unique properties to boost crop and livestock productivity (Batsmanova et al 2013; Scott and Chen 2013). There are several examples where the scientists have tested the efficiency of the nanoparticles in plant experiment and shown that there are significant increases in the physiological parameters of the plant, as compared to the conventional technologies. For the significant results, the foresight and patience are essential for applying nanotechnology in agriculture because generation of data in most agricultural fields is time-consuming and expensive, and success is uncertain due to the involvement of a large number of variables in farm production systems and because of the complex intrinsic relationship between nanomaterials and nature. It is worthwhile to recognize that a large number of nanomaterials have existed since time immemorial in soils, plants, and the atmosphere (Li et al. 2012; Wilson et al. 2008; Theng and Yuan 2008).

The traditional practices used for the seed germination, plant growth promotion and crop improvement, including breeding and use of microbial inoculation was now being reported successfully replaced by the application of carbon nanotubes as regulators of seed germination and plant growth (Khodakovskaya et al. 2013; Zheng et al. (2005). Thus, there are several such examples showing that there is the start of new genera, with the use of nanotechnology as the effective tool, which can be used in the field of plant growth and improvement.

Similarly, in disease management technologies, such as bacteriophages and systemic acquired resistance inducers, have been under investigation for several years as alternatives to Cu bactericides (Obradovic et al. 2005; Huang et al. 2012). Additional, the use of Bacteriophages, have also shown promising as biological alternatives to conventional Cu bactericides. However, ensuring the efficacy of bacteriophages is challenging in field conditions due to limited phage viability and the specific environmental requirements for their multiplication. In recent years, nanotechnology has been increasingly applied to the development of novel antimicrobials for the management of pathogenic bacteria affecting agricultural crops, humans and animals. In particular, significant development in nanomaterials synthesis, such as polymers, carbon-based and metallic, has attracted researcher's attention towards applications in managing plant diseases caused by bacteria. Toxicity considerations, including negative environmental effects, have also led to the redesign of nanomaterials by tuning the size and shape and by surface modification, leading to increased antimicrobial activity and decreased ecological toxicity (Neal 2008; Dasgupta et al. 2016a, b, c; Ranjan et al. 2014, 2015, 2016; Maddineni et al. 2015; Dasgupta et al. 2015; Jain et al. 2016).

9.7 Risk Assessment of Nanotechnology

The purpose of every newly developed mechanism is facilitated to the complex system and the welfare of the society. The development of nanotechnology is aiming to reduce size and improvement in the functionality of any application, but the safety of society is on high priority. The nanoparticles have a natural tendency to group together to form large particle which is called agglomeration. (Ostiguy et al. 2006), but for their application purpose they are required in unagglomerate form or individual particle form. Similarly the surface of nanoparticles is also modified for specific use by chemicals. In such context the manufacturer uses post synthetic strategies to prevent aggregation of particles. Uses of those chemicals and surface modifier materials have a major impact on the safety and toxicity of nanomaterial (Rana and Kalaichelvan 2013).

Therefore, the Eco-toxicity study is advised, as these includes natural uptake mechanisms and the influence of environmental factors on bioavailability. Nanotechnology is applied in different areas which have a direct relation to living beings such as health care and agriculture sector (Nel et al. 2009). Thus the use of nanotechnology improving the quality of life, but the impact of nanotechnology on human health is also a major concern regarding human health and the environment. Use of nanomaterial in agriculture is the direct root of entry of nanoparticle into soil system and plants and after consumption, in living beings. So there is need to determine the impact assessment of manufactured nanomaterials.

The effect of nanoparticles on in biological and chemical environment is determined by different factors such as size of the nanoparticle, chemical composition, surface chemistry, pH, ionic strength and ionic composition of environment, hydrodynamic condition and residence time (Ray et al. 2009)**.** Nanoparticles have size in the range of 1–1000 nm. Small nanoparticles have fast diffusion rate and easy to coagulate on large particles, deposit on the surface and facile binding with biological components.

In a review article by Auffan et al. (2009) explained the toxicity assessment of nanoparticles in chemical and biological environment. The effect of nanoparticle accumulation in the plant is very less studied and their impact on agriculture crops has been deliberate only in vitro: hydroponics (López-Moreno et al. 2010; El-Temsah and Joner 2012; Stampoulis et al. 2009; Kumari et al. 2009; Lin and Xing 2007), agar culture medium (Lee et al. 2008) and in Hoagland medium (Schwabe et al. 2013). Very less crops have evaluated for nanomaterial toxicity and their accumulating studies such as wheat, cucumber, corn, onion, pumpkin, tomato, rice, soyabean, lettuce and tobacco specially *Cucurbita pepo* and *Cucumis sativus* (Deng et al. 2014**;** Cui et al. 2014).

Nanoparticles journey starts in the food chain from soil via agriculture crop and its feeder and increase of bioaccumulation of nanoparticles in the food chain could be harmful for the environment (Zhu et al. 2008). It is reported that 20 nm sized TiO_2 nanoparticle is more toxic in comparison to 250 nm nanoparticles (Auffan et al. 2009). Similarly, 7 nm CeO_2 nanoparticles produced more oxidative stress in comparison to 300 nm sized nanoparticles and induce DNA and chromosome damage in vitro experiment. Different mechanisms such as transformation of chemical species, reactive oxygen species (ROS) development and toxic ion release play important role in toxicity of inorganic nanoparticles (Auffan et al. 2009). The effect of functionalized and non-functionalized carbon nanotubes were studied by Cañas et al. (2008) on cabbage, carrot, cucumber, onion, lettuce and tomato. They were found that in tomato non-functionalized carbon nanotubes inhibit root growth, but the enhancement in cucumber and onion, while functionalized carbon nanotubes inhibit the root growth in lettuce. Rest two crops were unaffected with both types of carbon nanotubes. Similarly, Yang and Watts (2005) reported that alumina nanoparticles showed inhibition of root at 2000 ppm concentration in corn, cucumber, soybean, cabbage and carrot, while Lin and Xing (2007) used multi walled nanotubes, zinc, zinc oxide alumina and aluminium to check their toxicity in rape, radish, lettuce, corn and cucumber and reported that only zinc and zinc oxide inhibit the seed germination. Shaw and Hossain (2013) reported the presence of CuO nanoparticle showed impaired germination and growth by oxidative damage. Similarly Dimkpa et al. (2013) and Shaw et al. (2014) showed the negative impact of CuO nanoparticle on wheat, maize and barley growth reduction and change in DNA integrity also have correlated with toxicity of CuO nanoparticle in radish, rye grass and buckwheat (Lee et al. 2010**;** Atha et al. 2012).

9.7.1 Accretion of Nanoparticle in Chemical and Biological Environment

Transportation, adsorption and accumulation of nanoparticles in agriculture crops depends on plant species and nanoparticle type, their interaction, size, chemical composition and long term stability of nanoparticle (Rico et al. 2011). The comparative study of different metal oxides (CeO_2, Fe_2O_3, SnO_2 and TiO_2 nanoparticle) and Ag, Co and Ni metal nanoparticles on tomato plant were carried out by Antisari et al. (2015). They reported that SnO_2 decreased the dry biomass up to 63.1 % and accumulation of Ag, Co and Ni nanoparticle occurred in root, stem and leaves of the plant additionally, Ag nanoparticle in fruit too. They concluded that size, shape, type of nanoparticle and surface chemistry is responsible for uptake, translocation and occurrences of nanoparticles in different organ. In contrast, nanoparticle also have advantageous role of absorbing the pollutant and reduce the toxicity by decrease the free concentration of pollutants in the environment (Nowack and Bucheli 2007).

The engineered nanoparticles usually occurred in agricultural field due to use of nanoparticles containing agrochemical or nano-formulations for crop protection and production improvement. When engineered nanoparticle release in to the environment they persist in air, water and soil after discharge and plant root is directly exposed to engineered nanomaterial present in soil and irrigation water, while leaves and stem tissue come in direct contact with atmospheric nanoparticles. The interaction of engineered nanoparticle in a biological environment with different type of biomolecules such as cellular organelles, lipid, nucleic acid and protein is basically depends on size and surface reactivity of nanoparticle (Auffan et al. 2009; Fadeel et al. 2007).

Zhang et al. (2011) reported that different type of interaction phenomena used such as electrostatic, mechanical adhesion, adsorption and hydrophobic affinity by engineered nanoparticles. In the cell the pore size of cell wall presents is in the range of 5–20 nm (Tepfer and Taylor 1981), nanoparticle or their cluster less than the pore size of cell wall could diffuse through pore and enter via symplastic or apoplastic flow. Sometimes nanoparticle sorption on to root surface create a structural damage and enter into the root tissue also, from there nanoparticles diffuse in space between the cell wall and plasma membrane (intracellular space) (Lin and Xing 2008). Engineered nanoparticles enter into inter cellular space through apopalstic pathway. Similarly, through apoplast (through cell wall), particles may enter in to epidermal and cortical cell to reach endodermis and accumulate there and sometime form aggregates of engineered nanoparticles, because waxy Casparian strip work as barriers for further movement of nanoparticles in the vascular system (Larue et al. 2012; Zhao et al. 2013a).

On the other hand Rico et al. (2011) hypothesized that symplastic (through cytoplasm) route is more organized and regulated pathway for movement of engineered nanoparticles in to plants. They proposed that binding of nanoparticle with carrier protein is helpful in cell internalization and easy to move through ion channels, aquaporins and endocytosis. In the experiment carried out by Khodakovskaya et al. (2012) supported the hypothesis by reported that presence of nanoparticles, expression of aquaporin proteins enhanced along with up regulation of water channel genes. Li et al. (2008) and Stark (2011) reported that in the interaction of nanoparticles also depend on hydrophobic and hydrophilic nature of particles. Hydrophobic nanoparticle embedded into the hydrophobic core of membrane without any damage, but hydrophilic nanoparticles absorb on the surface of the membrane. In the cell, nanoparticle surrounded by different type of biomolecules, forms a corona and smaller nanoparticle complex move through plasmodesmata to neighboring cells.

The effect of nanoparticles on cell internal structure in plants has been studied. Wang et al. (2011) and Larue et al. (2012) reported that during intercellular movement through plasmodesmata TiO_2 nanoparticles showed toxicity and disturb the micro tubular network in *Arabidopsis thaliana*. Additionally, Cifuentes et al. (2010) hypothesized that the presence of Rab protein determined the movement to specific areas near plasmodesmata. Transportation of engineered nanomaterial through simplistic flow showed highly effective into stele and then vascular tissue.

The toxicity by nanoparticle basically depends on generation of reactive oxygen species (ROS). When nanoparticles exposed to the light they generate excited electrons by photochemical response. These electrons form superoxide radicals in the presence of oxygen. Such situation where the organism exposed to light and nanoparticles, the simultaneous could be toxic to the organism (Cañas et al. 2008). Recently lot of work has been going on the mobility of nanoparticle into the environment, but more important is how they behave within the chemical or biological environment (Nowack and Bucheli 2007).

The biggest challenge is to find that in what concentration these engineered nanoparticles are beneficial or after what quantities they show toxicity in the environment. Presence of nanoparticles in the soil might be interacted with microbial community and effected microbial dynamics, soil ecosystem and carbon sequestering. Further, they can be influence different functional assay such as the decomposition of organic matter, nitrogen transformation and mycorhizal association. Still the research on interaction of engineered nanomaterial with soil microbial community and crop, transmission of engineered nanoparticles from plant to human begins and interaction with soil pollutant is very limited, so to understand the assessment of nanomaterial on ecosystem required more knowledge on engineered nanoparticles and crop interaction, safety of food products derived from the nanomaterial containing environment.

9.8 Conclusion

Nanotechnology is a fascinating technology, a door for the next revolution in the field of agriculture and Agri-technology. It can reduce the amount of chemical inputs to enhance the agricultural productivity and develop a healthy relationship between chemical inputs with eco-balance. Reduction of chemical fertilizer and pesticide is very much required for a sustainable future. Continuous uses of uncontrolled chemicals are disturbing the environment, microbial diversity, geo-biological cycles and human health. Long time residues of such inputs also affected the soil health and their nutrition system. So sustainability of nature is much required for our future generation and using nanotechnology we can control the chemical disaster in the agriculture field. The use of encapsulated and metal nanoparticle have been evidenced their promising approach in agriculture as fertilizer and pest control agents. The site specific feature and controlled release capacity of these carriers makes them more advantageous in agriculture. Their use as biosensor also will change the conventional farming practices and convert it into precision farming, which will provide the information about soil health, pest and nutritional requirement of the crop and helpful to reduce excessive input and agricultural cost and develop the smarter agriculture practice. On the other side, we need to assess the impact of nanotechnology in agriculture before commercialization of products. Accumulation of nanomaterial and their adverse effect on the environment is also a major concern. These nanoparticles showed toxicity after a certain limit against plant and human health. It is important more research is required for environmental impact assessment of nanomaterial and determine the non-toxic concentration for each crop.

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Chapter 10
Nanoparticles, Soils, Plants and Sustainable Agriculture

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Abstract Humanity faces major challenges involving energy, water, food, environment, poverty, diseases, education, democracy and population. Green nanotechnology could be a solution for providing sustainable energy, clean water and a better environment. Various nanomaterials can sustain the agricultural sectors. Here we review the applications of nanoparticles for soil security and plant nutrition.

Keywords Nanoparicles • Terrestrial environments • Sustainable agriculture • Soil security • Plant nutrition

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10.1 Introduction

Green nanotechnology is the nascent area of research involving the design of nanoscale substances, materials, and processes through green chemistry and green engineering that results in the development of new performance without adverse consequences to humans and the biosphere (McKenzie and Hutchison 2004). It has been said that green nanotechnology in its simplest form is preserving the applications while minimizing or eliminating the negative implications of nanomaterials (Eckelman et al. 2008). It could be noted that this kind of nanotechnology is (1) environmentally benign and sustainable, (2) is intended to contribute to the solution of some environmental problem or (3) at a minimum it should perform better than alternative non-green nanotechnologies (Geoffrey and Granqvist 2011). Recently, several publications focused on the field of green nanotechnology (e.g., McKenzie and Hutchison 2004; Eckelman et al. 2008; Dhingra et al. 2010; Geoffrey and Granqvist 2011; Guo 2012; Virkutyte and Varma 2013; Rickerby and Morrison 2014; Basiuk and Basiuk 2015).

Literally nanotechnology means any technology on a nanoscale that has applications in the real world (Bhushan 2010). The term "nanotechnology" was invented by Professor Norio Taniguchi at the University of Tokyo in 1974 with the following definition: *Nano-technology is the production technology to get the extra high accuracy and ultra fine dimensions*, i.e. *the preciseness and fineness on the order of* 1 nm (*nanometer*), 10^{-9} *m in length.* According to NASA's definition, "*nanotechnology is the creation of functional materials, devices and systems through control of matter on the nanometer length scale* (1–100 *nanometers*)*, and exploitation of novel phenomena and properties* (*physical, chemical, biological, mechanical, electrical…*) *at that length scale*" (Meyyappan 2004). It could be defined nanotechnology as a promising field of interdisciplinary research. It can open up a wide array of opportunities in various fields like agriculture, pharmaceuticals, medicine and electronics. Therefore, the potential benefits and uses of nanotechnology are enormous. Concerning the application of nanotechnology to agriculture is also getting attention nowadays (Prasad et al. 2014; Shapira and Youtie 2015; Resham et al. 2015; Nath 2015). It has been widely recognized that, reducing the impact of industry on the environment as an important priority for achieving sustainability. As a consequence, products and production methods are being modified, supply chains are evolving and increased attention is paid to the disposal of waste and recycling. Therefore, nanotechnology can play a key role in these developments because it has the potential to confer substantial societal, economic, and environmental benefits through more efficient energy generation and storage systems, reduction of emis-

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sions, resource saving, and substitution of hazardous substances (Rickerby and Morrison 2007; Rickerby and Morrison 2014). In developing countries, a large proportion of people face daily food shortages as a result of environmental impacts or political instability, whereas in the developed world there is surplus of food. The drive for developing countries is to develop drought and pest resistant crops, which also maximize yield. The potential of nanotechnology to revolutionize textile, materials, information and communication technology, the health care and energy sectors has been well publicized (Prasad et al. 2014).

Therefore, the role of nanoparticles in enhancing soil security, different effects on plants as well as the significance of these nanoparticles for plant nutrition and hence sustainable agriculture will be highlighted.

10.2 Nanoparticles for Sustainable Agriculture

Humankind faces a lot of challenges. These challenges can be listed according to Nobel Laureate Richard E. Smalley (1996) including the following top ten problems: (1) energy, (2) water, (3) food, (4) environment, (5) poverty, (6) terrorism and war, (7) disease, (8) education, (9) democracy, and (10) population. Furthermore, it could be used this list according to the green nanotechnology for providing energy, clean water and a good environment in a sustainable way (Geoffrey and Granqvist 2011). It could be noticed that, about 50 % from these previous challenges in close relation with the agriculture.

Starting with agriculture, it is the basic activity by which humans live and survive on the Earth (Reddy 2015). This activity has a lot of systems including conventional, conservation or sustainable and organic agricultural systems. Concerning conventional agriculture, it has largely been characterized by tillage, which leaves soil vulnerable to erosion. It could be also characterized by minimal soil disturbance, diversified crop rotations, and surface crop residue retention to reduce soil and environmental degradation while sustaining crop production. These both tillage and crop residue burning as conventional farming practices have substantially degraded the soil resource base, with a concomitant reduction in crop production capacity. Due to the conventional farming practices, continued loss of soil is expected to become critical for global agricultural production. This conventional mode of agriculture through intensive agricultural practices achieves production goals, but simultaneously degrades the natural resources (Farooq and Siddique 2015).

On the other hand, conservation agriculture is a new paradigm for achieving sustained agricultural production and is a major step in the transition to sustainable agriculture. Conservation agriculture is widely recognized as a viable approach to creating a sustainable agriculture (Farooq and Siddique 2015). It is a resource-saving agricultural production system that aims to achieve production intensification and high yields while enhancing the natural resource base through compliance with four interrelated principles viz. minimal soil disturbance, permanent residue cover, planned crop rotations and integrated weed management, along with other good production practices of plant nutrition and pest management. Conservation agriculture is a set of technologies, including minimum soil disturbance, permanent

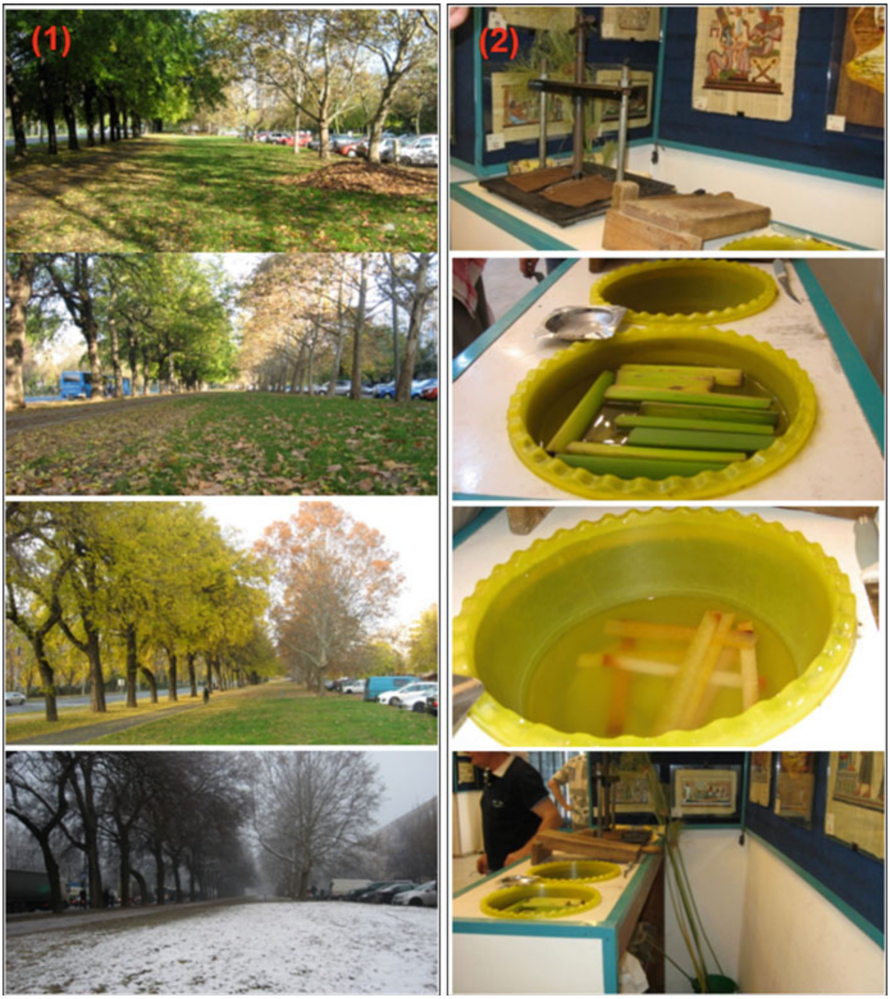

Fig. 10.1 Plants can sustain our life: composting from leaves (from September till snowing by February in Böszörményi Street, Debrecen, Hungary; photo 1), whereas photo 2 represents some steps explaining how the ancient Egyptian used the papyrus plant (*Cyperus papyrus*) for making papyrus paper (Photos by El-Ramady)

soil cover, diversified crop rotations, and integrated weed management (Friedrich et al. 2012), aimed at reducing and/or reverting many negative effects of conventional farming practices such as soil erosion, soil organic matter decline, water loss, soil physical degradation, and fuel use (FAO 2008; Farooq and Siddique 2015).

Therefore, the growing concerns for sustainable agriculture are in response to the limitations of both low-input, traditional agriculture and intensive modern agriculture relying on high levels of inputs for crop production (Figs. 10.1 and 10.2). Sustainable agriculture relies on practices that help to maintain ecological equilibrium and encourage natural regenerative processes such as nitrogen fixation, nutrient cycling, soil regeneration, and the protection of natural enemies of pest and

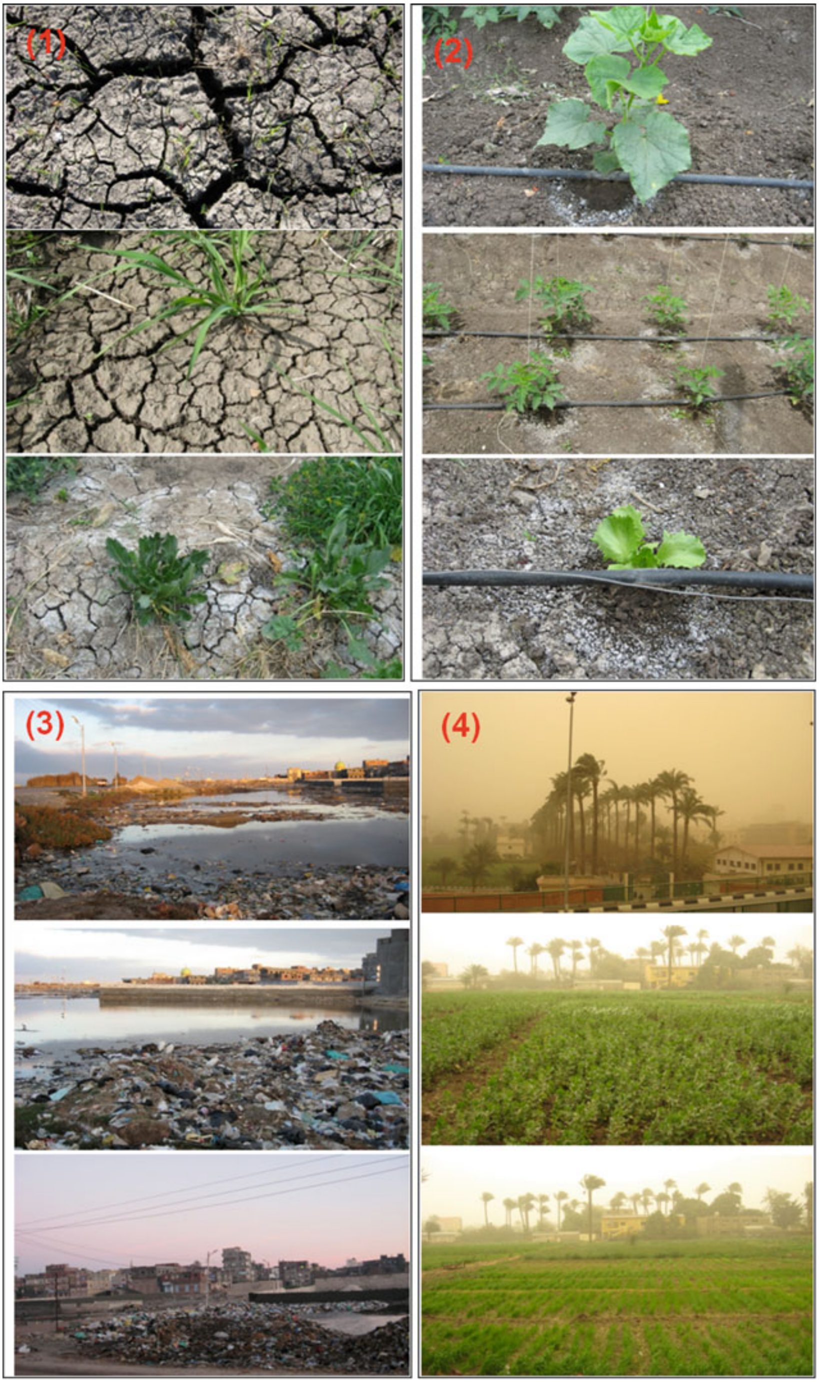

Fig. 10.2 Soils suffer from salinity and/or alkalinity (salt-affected soils) in field (photo 1) or in green house under drip irrigation (photo 2), pollution and water logging in Kafr El-Sheikh (photo 3) and sandy storm on February 11, 2015 (photo 4) in Giza (Photos by El-Ramady)

diseases as well as the targeted use of inputs. Agricultural systems relying on such approaches not only support high productivity, but also preserve biodiversity and safeguard the environment (Farooq and Siddique 2015).

Concerning nanoparticles and its behavior in frame of sustainable agriculture, it is an emerging issue all over the world. Whereas, there are several publications including book chapters, reviews, books such as Anandaraj et al. (2011), Chen and Yada (2011), Ditta (2012), Prasad et al. (2012, 2014), Tarafdar et al. (2013), Thul et al. (2013), El Beyrouthya and El Azzi (2014), Takeuchi et al. (2014), Mukhopadhyay (2014), Ngô and Van de Voorde (2014), de Oliveira et al. (2014), Wigger et al. (2015), Ditta et al. (2015), Thul and Sarangi (2015), Patil et al. (2016), Salamanca-Buentello and Daar (2016), Hasegawa et al. (2016), and Lourtioz et al. (2016). It is worth to mention that, recently the American Chemical Society published some publications concerning this subject e.g., Shamim and Sharma (2013), Doong et al. (2013), Park and Appell (2013), and Hu et al. (2014a).

Regarding to soil, it is biogeochemically dynamic entities that play an important role in sustaining life forms within the Earth's critical zone by regulating processes in terrestrial ecosystems. Furthermore, soils can provide critical support essential for life on the earth, regulate processes across diverse terrestrial ecosystems, and interact with the atmosphere (Adewopo et al. 2014). Concerning the most important and emerging research area in soil sciences, it is well established some thematic areas for this subject including soils as a key regulator of ecosystem functions, role of soils in public health and human well-being, soils mediating nutrient cycling, transport processes, and plant-soil – microbial interactions, soil formation and degradation and soil information systems (Figs. 10.1 and 10.2). Therefore, identifying priority research challenges within a scientific area is a daunting task, but the outcomes could present unparalleled opportunities for advancing the science. However, the uniqueness of soil science lies in its rich blend of biology, chemistry, pedology, physics, mathematics, and social sciences as well as communication (Adewopo et al. 2014).

Therefore, it could be concluded that, nanoparticles or nanomaterials can be used in sustaining the agricultural sectors including food, energy, water, and soils, within food security, energy security, water security and soil security. We should broaden our view on nanoparticles or nanomaterials considering different potentials for a sustainable materials management.

10.3 Enhancing Soil Security

Soil security has been defined in analogy with food security, which aims at the long term sustainable production of sufficient quantities of food, providing a permanent feeling of security to world citizens. This implies, however, much more than striving for a higher production as such, as many socioeconomic, institutional, and ethical aspects also play a key role (Bouma et al. 2015). The security concept is more complicated when applied to soils. Rather than relate to a sustainable, daily need in terms of food intake, soil security relates to what might happen if soils degrade to the extent that sufficient food production is not feasible anymore. Soil degradation is a long-term process, very much related to varying socioeconomic conditions. Except for erosion, its effects are often gradual and difficult to communicate and translate into environmental and economic values. However, when soils degrade to the extent that they cannot anymore provide certain ecosystem services, of which food production is only one provisioning service, the consequences for society are devastating. To mitigate degraded soils is very difficult and even impossible when soil has been removed by erosion. The challenge, therefore, is to create early awareness about the dangers of soil degradation that may, in the end, terminate many ecosystem services the soil can provide (Bouma et al. 2015).

A side from soil security, food security was and will remain a major among global issues of the twenty-first century. Furthermore, principal determinants of food security include the availability and quality of soil resources, and their interactions with water resources as well as vegetation (crop species) through energy-based inputs using managerial skills for optimizing the net primary productivity (Lal 2015). This net primary productivity is specifically affected by critical linkages that govern some specific functions of nexuses. These nexuses include the first one, soil and water for the plant, available water capacity by influencing water retention and transmission, conversion of blue and grey into green water, and moderating the effects of pedologic and agronomic droughts (Lal 2015). The second includes soil and vegetation for biogeochemical cycling, which determines elemental budgets (i.e., C, N, P, and S), nutrient use efficiency, root distribution and turnover and soil/root respiration. Whereas, the third is vegetation and energy for energy/mass transformation and influencing energy productivity, ecosystem C budget, and biomass feedstocks for biofuel production. Finally, the fourth one is energy and water affecting the hydrological cycle with specific impacts on water and energy balance on a landscape, energy use in irrigated systems, and moderation of the hydrological/meteorological droughts. These nexuses affect and are affected by climate changes and variability on the one hand and anthropogenic perturbations (human demands) on the other (Lal 2015).

Lal (2015) reported about the importance of nexuses and their inter-connectivity. He mentioned that, there is a close relationship between soil security, water security, climate security, energy security, economic security and political security. Concerning the food security, it includes availability, access, nutritional quality, and retention, which strongly depends on soil security (quality, resilience), water security (quality, renewability, availability), energy security (dependability, supply, price), climate security (optimal temperature and moisture regimes, and low frequency of extreme events), economic security (income and access to resources), and political stability (peace and harmony). Therefore, the co-productivity generated by the anthropogenic use of primary resources (soil, water, climate) and secondary inputs (amendments, fertilizers, irrigation, tillage) must be optimized. Understanding and judiciously managing the water-soil-waste nexus for food security is important to enhancing human wellbeing, achieving the sustainable use of natural resources, improving the environment and sustaining ecosystem functions and services (Lal 2015).

10.4 Nanoparticles and Plants

Nanotechnology is a new emerging and fascinating field of science. Nanotechnology permits advanced research in many areas and nanotechnological discoveries could open up novel applications in the field of biotechnology and agriculture (Siddiqui et al. 2015a). Nanomaterials, as a term is based on the prefix “nano,” which originates from the Greek word meaning “dwarf.” More precisely, the word nano means 10^{-9} or one billionth of a meter (Huang et al. 2015). The word nanomaterial is generally used for materials with a size ranging between 1 and 100 nm (Rai and Ingle 2012). Generally, nanomaterials refer to a colloidal particulate system, in which size ranging from 10 to 1000 nm, possessing unique properties, such as size dependent qualities, high surface-to-volume ratio, and promising optical properties (Aslani et al. 2014). It could be also defined nanoparticles, which refer to a category of nanomaterials, a submicron or even ultramicron size particles obtainable as high performance radiant resistant materials, magnetic materials, solar battery materials, packaging materials, and magnetic fluid materials (Aslani et al. 2014). Furthermore, it could be divided nanoparticles into natural and anthropogenic (manufactured or engineered) particles. Depending on their chemical composition, these particles can be further separated into carbon-containing and inorganic nanoparticles. Hence, the C-containing or inorganic nanoparticles can be formed using biogenic, geogenic, atmospheric and pyrogenic processes (Nowack and Bucheli 2007).

Due to their great surface area per mass unit, nanoparticles are expected to be more biologically active than larger sized particles of the same chemical composition (Sozer and Kokini 2009). Beside a very large specific surface area, nanoparticles high unique properties including surface energy, and quantum confinement (Ma et al. 2010). These unusual properties may result in substantially different environmental fate and behaviors than their bulk counterparts. Hence, an emerging area of research nowadays is focused on short and medium term studies of the environmental and ecological impact of released nanoparticles. Due to the interaction between nanoparticles and plants, many morphological and physiological can be changed, depending on the properties of these nanoparticles (Siddiqui et al. 2015b). Furthermore, efficacy of these nanoparticles is determined by their chemical composition, size, shape, surface covering, reactivity, and most importantly the dose at which they are effective in the terrestrial environments (Khodakovskaya et al. 2012; Dasgupta et al. 2015, 2016a, b, c; Ranjan et al. 2014, 2015, 2016; Jain et al. 2016; Maddineni et al. 2015).

Several positive and negative effects of nanoparticles on plant growth and development have been already reviewed by many researchers from their findings (e.g., Nowack and Bucheli 2007; Ju-Nam and Lead 2008; Handy et al. 2008; Mueller and Nowack 2008; Stampoulis et al. 2009; Ruffini and Cremonini 2009; Kahru and Dubourguier 2010; Ma et al. 2010; Nair et al. 2010; Peralta-Videa et al. 2011; Menard et al. 2011; Khot et al. 2012; Pan and Xing 2012; Smita et al. 2012; Ma et al. 2013; Gardea-Torresdey et al. 2014; Deng et al. 2014; Aslani et al. 2014; Hudson and Roberta 2015; Huang et al. 2015; Siddiqui et al. 2015b; Chichiriccò and Poma 2015; Aliofkhazraei 2016; Abd-Alla et al. 2016; Gil-Díaz et al. 2016; Le Van et al. 2016; Wen et al. 2016). They found that, the impact of engineered nanoparticles on plants depends on the composition, concentration, size and physical and chemical properties of engineered nanoparticles as well as plant species. Efficacy of these engineered nanoparticles depends on their concentration and varies from plant to plant. However, this review covers plausible role nanoparticles in seed germination, plant growth (shoot and root biomass) and photosynthesis.

A recent trend in nanotechnology has been known as nano-bio interactions to investigate the interactions of nanomaterials with biological systems like plants

(Albanese et al. 2012). Plant growth and development starts from the germination of seeds followed by root elongation and shoot emergence as the earliest signs of growth and development. Therefore, it is important to understand the plant growth and development in relation to nanoparticles. The reported data from various studies suggested that effect of nanoparticles on seed germination dependent on their concentrations. There are several authors studied the effects of nanoparticles on plants including many metals/metaloids or metal oxide such as:

1. Cerium (Zhao et al. 2013b, 2014; Rico et al. 2015; Hong et al. 2014),
2. Copper (Shaw and Hossain 2013; Ouda 2014; Lalau et al. 2014; Nair and Chung 2014; Perreault et al. 2014; Shi et al. 2014; Da Costa and Sharma 2015),
3. Gold (Zhai et al. 2014; Gunjan et al. 2014; Dan et al. 2015),
4. Iron (Ghafariyan et al. 2013; Faria et al. 2014; Pardha-Saradhi et al. 2014; Burke et al. 2015; Libralato et al. 2016),
5. Nickel (Faisal et al. 2013; Oukarroum et al. 2015),
6. Selenium (Domokos-Szabolcsy et al. 2012; Husen and Siddiqi 2014; El-Ramady et al. 2015a, b, c, 2016),
7. Silicon (Li et al. 2012; Suriyaprabha et al. 2012a, b; Hussain et al. 2013; Siddiqui et al. 2014; Siddiqui and Al-Whaibi 2014; Kalteh et al. 2014; Roohizadeh et al. 2015; Wang et al. 2015b),
8. Silver (Kaveh et al. 2013; Silva et al. 2014; Larue et al. 2014a, b; Boenigk et al. 2014; Geisler-Lee et al. 2014; Ouda 2014; Meena and Chouhan 2015; Razzaq et al. 2016),
9. Titanium (Foltete et al. 2011; Gao et al. 2013; Burke et al. 2015), and
10. Zinc (Prasad et al. 2012; Pokhrel and Dubey 2013; Hu et al. 2014b; Zhao et al. 2013a, 2014; Tyagi et al. 2014; Bandyopadhyay et al. 2015; Vochita et al. 2016),

It could be listed some toxic and beneficial effects of both nano-SiO_2 and nano-ZnO in the following Tables (Tables 10.1 and 10.2). Concerning these effects, it could be concluded some findings as follows:

Table 10.1 Beneficiary concentration(s) of zinc and silicon nanoparticles for plants (Siddiqui et al. 2015b) comparing with nano-Se

Nanoparticle (plant species)	Beneficiary concentration	Part of plant/process	Reference(s)
Nano-ZnO (*Cucumis sativus*) fruit	400 mg kg^{-1}	Micronutrients: Cu, Mn and Zn	Zhao et al. (2014)
Nano-ZnO (*Cicer arietinum* L.)	1.5 mg kg^{-1} (foliar spray)	Shoot dry weight	Burman et al. (2013)
Nano-ZnO (*Vigna radiate*)	20 mg kg^{-1} (foliar spray, suspension)	Biomass	Dhoke et al. (2013)
Nano-SiO_2 (*Zea mays* L.)	15 kg ha^{-1}	Growth parameters	Yuvakkumar et al. (2011) and Suriyaprabha et al. (2012a)
Nano-Se (*Nicotinia tabacum* L.)	100 mg kg^{-1}	Callus initiation and microshoot formation	Domokos-Szabolcsy et al. (2012)
Nano-Se (*Arundo donax* L.)	100 mg kg^{-1}	Rooting and other growth parameters	Domokos-Szabolcsy et al. (2014)
Nano-Se (*Triticum aestivum* L.; *Raphanus sativus* L.)	100 mg kg^{-1}	Production of biofortified sprouts using micro-farm system	El-Ramady et al. (2016)

Table 10.2 Effect of nano-ZnO and nano-SiO_2 on germination and growth of some plants or microbes

Nano-particle	Crop/plant/microorganism	Comments (toxicity or enhancement according to nanoparticles concentration)	References
Nano-ZnO	Peanut (*Arachis hypogaea*)	Improved growth and yield (up to 1000 mg kg^{-1})	Prasad et al. (2012)
	Cluster bean (*Cyamopsis tetragonoloba* L.)	Improved shoot-root growth, chlorophyll (photosynthetic pigment), total soluble leaf protein content, rhizospheric microbial population, and P nutrient-mobilizing enzymes including phytase, acid and alkaline phosphatase (foliar up 10 mg kg^{-1})	Raliya and Tarafdar (2013)
	Ryegrass (*Lolium perenne*)	Reduced biomass, shrank root tips, epidermis and root cap broken, highly vacuolated and collapsed cortical cells (up to 1000 mg kg^{-1} in Hoagland solution)	Lin and Xing (2008)
	Cabbage (*Brassica oleracea* var. capitata L.)	Dose-dependent inhibition of germination in aqueous suspension (1000 mg kg^{-1})	Pokhrel and Dubey (2013)
	Bacteria (*Bacillus subtilis*) (*Escherichia coli*)	Mild toxicity due to reactive oxygen species (ROS) production (up to 5000 mg L^{-1})	Adams et al. (2006)
	Bacteria (*Pseudomonas putida*)	Inhibition of bacterial growth (up to 100 mg L^{-1})	Li et al. (2011)
	Bacteria (Rhizobiales, Bradyrhizobiaceae, Bradyrhizobium)	Decline in bacterial communities and reduced diversity (500 mg kg^{-1} soil for nano-ZnO)	Ge et al. (2012)
Nano-SiO_2	Maize (*Zea mays* L.)	Enhanced plant dry weight and levels of organic compounds such as proteins, chlorophyll and phenols (up to 15 kg ha^{-1})	Suriyaprabha et al. (2012a, b)
	Tomato (*Lycopersicum esculentum* Mill)	Improved seed germination (up to 8 g L^{-1})	Siddiqui and Al-Whaibi (2014)
	Mouse-ear cress (*Arabidopsis thaliana*)	Increased root length at 400 mg L^{-1}, but reduced root length at 2000 and 4000 mg L^{-1}	Lee et al. (2010)
	Lupin (*Lupinus sp.*) and wheat (*Triticum spp.*)	No signs of toxicity were observed and did not affect seed germination and did not show phytotoxicity (2000 mg L^{-1})	Hussain et al. (2013)
	Bacteria (*Bacillus subtilis*) (*Escherichia coli*)	Mild toxicity due to reactive oxygen species (ROS) production (up to 5 g L^{-1})	Adams et al. (2006)

Source: Ditta et al. (2015), Li et al. (2015), Mura et al. (2015), and Thul and Sarangi (2015)

(a) It is found that, the application of nano-SiO_2 (up to 8 g L^{-1}) significantly improved seed germination of tomato, seed germination index, seed vigor index, seedling fresh weight and dry weight. Due to this application of nano-SiO_2, an increase in germination parameters may be effective for the growth and yield of crops. It could be suggested that, nano-SiO_2 could be used as a fertilizer for the crop improvement (Siddiqui and Al-Whaibi 2014).
(b) It is also reported that, nano-SiO_2 enhanced seed germination and stimulated the antioxidant system under NaCl stress in case of tomato (Haghighi et al. 2012) and for squash (Siddiqui et al. 2014).
(c) Under salinity stress, nano-SiO_2 improves leaf fresh and dry weight, chlorophyll content and proline accumulation. Due to the application of nano-SiO_2, it is found an increase in the accumulation of proline, free amino acids, content of nutrients, antioxidant enzymes activity, thereby improving the tolerance of plants to abiotic stress (Haghighi et al. 2012; Li et al. 2012; Siddiqui et al. 2014; Kalteh et al. 2014).

Several studies suggested that, zinc oxide nanoparticles (nano-ZnO) increased plant growth and development such as peanut (Prasad et al. 2012), soybean (Sedghi et al. 2013), wheat (Ramesh et al. 2014) and onion (Raskar and Laware 2014). These previous authors reported that, lower concentration of nano-ZnO exhibited a beneficial effect on seed germination. It is also found using different concentrations of nano-ZnO on cucumber, alfalfa and tomato, that only cucumber seed germination was enhanced (de la Rosa et al. 2013). Helaly et al. (2014) found that, nano-ZnO (up to 200 mg L^{-1}) supplemented with MS media promoted shooting, somatic embryogenesis, regeneration of plantlets, and also induced proline synthesis, activity of some enzymes including superoxide dismutase, catalase, and peroxidase thereby improving tolerance to biotic stress. Therefore, some researchers have been studied different toxicological effect of nanoparticles on plants due to their unique properties. Whereas, their research focused on the realization of the beneficial effects of nanoparticles on plant remains incomplete. Furthermore, few studies have shown a positive effect of nanoparticles on plant growth and development. It is proved that, effect of nanoparticles varies from plant to plant depending on their mode of application, size and concentrations by Siddiqui et al. (2015b).

It could be concluded that, nanoparticles have different effects on plants depending on several factors including plant species, nanoparticles and environmental factors. Further research is needed to confirm whether nanoparticles are essential for plants as well as the current researches are in the beginning. To understand biochemical, physiological and molecular mechanisms of nanoparticles in plants, more hard works are required.

10.5 Nanoparticles for Plant Nutrition

The applications of nanotechnology concerning applied materials sciences and biomass conversion technologies can be considered the basis of providing food, feed, fiber, fire, and fuels in agriculture. Therefore in agriculture, management of

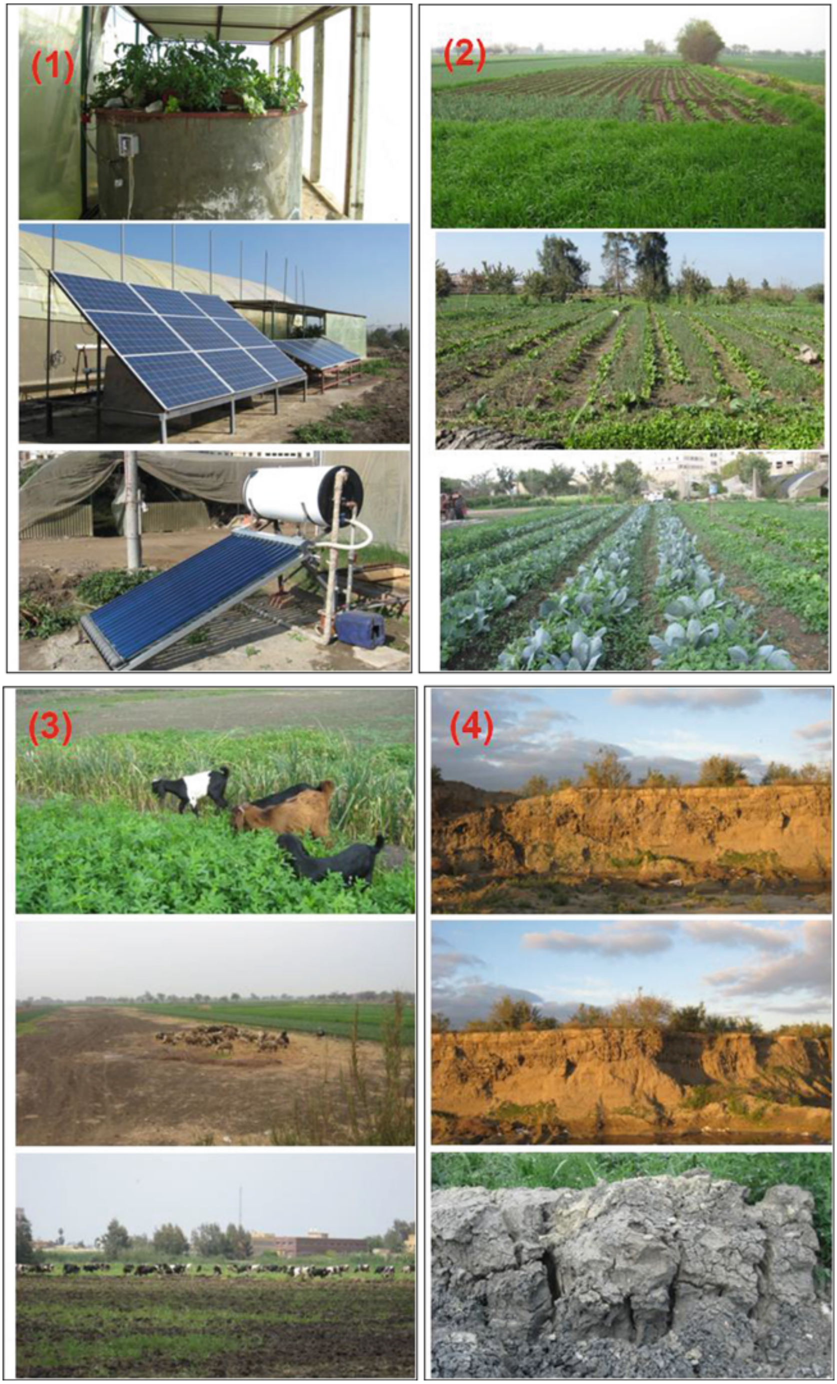

Fig. 10.3 Closed hydroponic system (vegetables and fish production) and solar energy system can be used in the experimentation farm in Kafrelsheikh Uni., (photo 1), intensive crop production (photo 2), livestock production system in Kafrelsheikh (photo 3) and sediments (NOT soil profile) from Burullus Lake (sandy soils) and main Gharbia drain (clay soils) during the cleaning process (photo 4) in Kafr El-Sheikh Governorate (Photos by El-Ramady)

Fig. 10.4 Soil management of salt-affected soils can be performed in strawberry (photo 1) and pepper (photo 2) production under green house (drip irrigation), to overcome their problems using soil amendments and solarization in Kafrelsheikh Uni (Photos by El-Ramady)

optimum plant nutrients for sustainable crop production is the priority-based area of research (Figs. 10.3 and 10.4). In this regard, much progress in the area of plant nutrition has come forward and nano-nutrition is one of the most interesting research areas for sustainable agriculture production (Ditta et al. 2015). Plant nano-nutrition is the application of nanotechnology for the provision of nano-sized nutrients for the crop production. It could be used of nanoparticles or nano-nutrients under two cases including biotic and abiotic forms. In regard to the abiotic form of nano-nutrients, it is prepared from inorganic sources like salts but due to many of them non-biodegradable, it is not safe. Concerning the biotic one, it is prepared from organic sources which are definitely environment friendly and biodegradable (Ditta et al. 2015). Therefore, a few attempts or studies have been made in the field of nano-nutrition and a lot more are expected in the near future because this field of plant nutrition is efficient and sustainable. Hence, it could be increased the efficiency of micro- as well as macro-nutrients for plants using this nano-nutrition (Ditta et al. 2015; Mastronardi et al. 2015; Servin et al. 2015; Thul and Sarangi 2015).

It is well documented that, nanotechnology has the potential to revolutionize the agricultural sector with novel tools for enhancing the productivity of the crop plants through efficient nutrients in the form of nanofertilizers, nanopesticides, or nanoherbicides by the plants (Tarafdar et al. 2013). Whereas, it could be enhanced the agricultural productivity by using of such nano-nutrients for formulation of nanofertilizers, nano-porous zeolites for slow release, enhanced germination, as well as efficient nanocapsules for herbicide delivery and vector; efficient dosage of water and fertilizer; pest management and nano-sensors for pest detection (Scrinis and Lyons 2007). These previous applications would definitely be helpful for the solutions of the limitations and challenges facing large scale and intensive farming systems (Ditta et al. 2015).

It is also reported that, nanomaterials have great implications in sustainable agricultural crop production and many studies reported their positive impact on various crops, whereas the main effect has been reported to be improved in these reports is the germination of various crops (Ditta et al. 2015). Concerning this effect on the germination of plants, some studies have been involved in improving the growth of crops by the application of different nano-nutrients such as nano-SiO_2 in maize and tomato (Suriyaprabha et al. 2012a, b; Siddiqui and Al-Whaibi 2014), carbon nanotubes in tomato, mustard and rice (Khodakovskaya et al. 2009; Nair et al. 2010; Ghodake et al. 2010), nanao-TiO_2 in spinach and wheat (Lei et al. 2008; Feizi et al. 2012; Larue et al. 2012), and nano Si, Pd, Au, Cu in lettuce (Shah and Belozerova 2009). Therefore, it could be summarized the effects of nanonutrients or nanofertilizers on the growth, germination rate, phytotoxicity and other physiological characterizations for certain common vegetable and field crops as follows:

1. Barley (*Hordeum vulgare* L.): Chauhan et al. (2013), Gruyer et al. (2014), Rico et al. (2015), and Feichtmeier et al. (2015);
2. Chickpea (*Cicer arietinum* L.): Burman et al. (2013), Mohammadi et al. (2013, 2014), Nair and Chung (2015b), and Hasanpour et al. (2015);
3. Cabbage (*Brassica pekinensis* L.): Baskar et al. (2015) and Xiang et al. (2015);
4. Cucumber (*Cucumis sativus* L.): Kim et al. (2012), Shams et al. (2013), Cui et al. (2014), Haghighi and da Silva (2014), and Zhang et al. (2015);
5. Green pea (*Pisum sativum* L.): Huang et al. (2014), Mukherjee et al. (2014), and Nair and Chung (2015a);
6. Lettuce (*Lactuca sativa* L.): Song et al. (2013), Gruyer et al. (2014), Gui et al. (2015b), Doolette et al. (2015), Hong et al. (2015), and Zahra et al. (2015);
7. Maize (*Zea mays* L.): Suriyaprabha et al. (2012a, b), Sun et al. (2014), Liu et al. (2015), and Zhang et al. (2015);
8. Oil seed rape (*Brassica napus* L.): Song et al. (2013), Kouhi et al. (2015a, b), Palmqvist et al. (2015), and Sarabi et al. (2015);

9. Onion (*Allium cepa* L.): Golubkina et al. (2012), Haghighi and da Silva (2014), Laware and Raskar (2014), Konotop et al. (2014), and Taranath et al. (2015);
10. Rice (*Oryza sativa* L.): Nair et al. (2011), Shaw and Hossain (2013), Rico et al. (2013a, b), Gui et al. (2015a), Da Costa and Sharma (2015), and Wang et al. (2015b);
11. Tomato (*Solanum lycopersicum* L.): Haghighi et al. (2012), de la Rosa et al. (2013), Faisal et al. (2013), Haghighi and da Silva (2014), Siddiqui and Al-Whaibi (2014), Shankramma et al. (2015), Antisari et al. (2015), and Mehrian et al.(2015);
12. Turnip (*Brassica rapa* ssp. rapa L.): Thiruvengadam et al. (2015);
13. Wheat (*Triticum aestivum* L.): Du et al. (2011), Larue et al. (2012), Feizi et al. (2012), Cui et al. (2014), Yanık and Vardar (2015), Wang et al. (2015a), and Watson et al. (2015).

An increase in the germination rate of the previous stated crops is an important aspect of the nanomaterials however, the application of these nanomaterials as a nutrient source for the entire growth cycle of two crop plants needs to be explored yet. So, the evaluation of these materials as a nutrient source, their critical concentration, and their phytotoxic effects, if any need to be explored in future (Ditta et al. 2015).

Recently, several studies have been focused on the interaction between nanoparticles and different plant species including the physiological, phytotxicological and biochemical aspects as well as plant nutrition (Patra et al. 2013; Seabra et al. 2014; Taran et al. 2014; El-Ramady et al. 2014a, b, 2015b, c, d, 2016; Ditta et al. 2015; Subramanian et al. 2015; Dimkpa et al. 2015; Da Costa and Sharma 2015, Mastronardi et al. 2015; Monreal et al. 2015; Solanki et al. 2015). So, plant nanonutrition and nanofertilizers as well as nanophytoremediation are emerging issues should be considered in frame of sustainable agriculture. Extensive studies had been undertaken to study different nanoparticles containing nutrients in frame of plant nutrition as follows:

1. Nitrogen-nanofertilizers (Subramanian and Sharmila Rahale 2013; Mohanraj 2013; Manikandan and Subramanian 2014; Seabra et al. 2014),
2. Phosphate-nanofertilizers (Bansiwal et al. 2006; Adhikari 2011; Behnassi et al. 2011; Liu and Lal 2014),
3. Potassium-nanofertilizers (Subramanian and Sharmila Rahale 2012),
4. Sulfur-nanofertilizers (Patra et al. 2013; Selva Preetha et al. 2014; Thirunavukkarasu 2014),
5. Calcium oxide nanoparticle (Deepa et al. 2015), iron oxide nanoparticle (Kim et al. 2015),
6. Magnesium nanofertilizers (Delfani et al. 2014),
7. Copper oxide nanoparticles (Da Costa and Sharma 2015; Dimkpa et al. 2015),
8. Manganese nanoparticles (Pradhan et al. 2014),
9. Zinc oxide nanoparticles (Subramanian and Sharmila Rahale 2012; Patra et al. 2013; Tarafdar et al. 2014; Dimkpa et al. 2014, 2015; Watson et al. 2015),

10. Silicon nanoparticles (Siddiqui and Al-Whaibi 2014; Kalteh et al. 2014; Le et al. 2014; Abdul Qados and Moftah 2015; Abdul Qados 2015),
11. Molybdenum (Aubert et al. 2012; Taran et al. 2014; Kanneganti and Talasila 2014),
12. Iron oxide (Alidoust and Isoda 2013; Ghafariyan et al. 2013; Lebedev et al. 2014; Soliman et al. 2015; Shankramma et al. 2015),
13. Nickel oxide (Faisal et al. 2013; Oukarroum et al. 2015; Antisari et al. 2015) and
14. Selenium nanoparticles (Golubkina et al. 2012; Husen and Siddiqi 2014; El-Ramady et al. 2015b, c, d, 2016; Papkina et al. 2015).

For more an efficient use of agricultural natural resources like water, nutrients, and chemicals during farming, nanotechnology (like nano-sensors) gave us the ability to develop and maximize the benefits of these resources management. Moreover, these nano-sensors, which have been proved to be user friendly, have not only been used as nano-biosensors but also for the control of soil nutrients and these have helped in the reduction of fertilizer consumption and environmental pollution (Ingale and Chaudhari 2013; Ditta et al. 2015; Kah 2015).

Therefore, it is well established that, nanotechnology has great potential in improving the quality of life through its applications in various fields including agriculture production and food system. Moreover, the nanomaterials have been applied as nano-nutrients (in the form of nanofertilizers) for crop production and as crop protectants in the form of nanopesticides and nano-herbicides, as well as nano-sensors in precision agriculture. In this regard, the importance of nano-nutrition in the sustainable agricultural production and its future scenario could be possible to apply on a large scale. Nevertheless, nanotechnology has a great potential in various walks of life, but we must be very careful about any new technology to be introduced for its possible unforeseen related risks that may come through its positive potentials. Therefore, potential applications of nanotechnology in agricultural production for the welfare of humans and hence sustainable environment, challenges, and opportunities for developing countries should be kept in mind.

It could be concluded that, nanoparticles are emerging issues for plant nutrition in the frame of sustainable agriculture. These nanoparticles can be considered an important source for nano-nutrition of plants and nanofertilizers. Otherwise, there are some open questions still in needing to answer including: (1) are nano-nutrients or nanofertilizers enough or sufficient sources for crop production instead of normal mineral fertilizers? (2) To what extent are the different effects of nanofertilizers currently taken into account? (3) Can different risks and benefits associated with the use of nanofertilizers be assessed? (4) Which nanofertilizer types are ready to emerge in the forseen future under different regulations?

10.6 Conclusion

The aim of this review is to explore the potential of the field of nanoparticles with respect to sustainable agriculture. This main focus is on the currently applied uses of nanoparticles for agriculture including different effects in enhancing soil security, using of nanoparticles for plant nutrition as well as nanoparticles and its effects on plants. Nanoparticles have emerged as a versatile platform, which could provide cost-effective, efficient and environmentally acceptable solutions to the global sustainability challenges facing society. Nanoparticles have a significant influence on the economy and the environment by improving both fertilizers and energy. So, these nanoparticles have a high potential for achieving sustainable agriculture. Therefore, the agri-nanotechnology might take a few decades to move from laboratory to land.

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