Ram Prasad · Vivek Kumar
Manoj Kumar *Editors*

Nanotechnology

Food and Environmental Paradigm

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Preface

The world around us is changing, there is growing awareness of the state of the environment, and there is developing concern due to the overexploitation of natural resources by mankind. Reduction of food and other resources combined with population growth can lead to hunger. This “new world” has led the nanotechnology to promise to a responsible role in preserving the environment for future generations and, while doing so, to continuously explore for ways to increase sustainable food and environmental resources. The increasing uses of nanoparticles pose challenging issues of safety for the environment and human activity.

Phytoengineered nanomaterials from plants are gaining consideration due to their cost-effective, sustainable, resource-efficient, simplicity, and eco-friendly nature. In this book entitled *Nanotechnology*, the editor has accrued numerous advanced approaches for studying the food and environmental science for the benefit of humankind. The book covers a wide range of aspects in the application of nanomaterials, synthesis of biogenic nanoparticles, the mechanism involved in the biosynthesis, and a unique template for synthesis of tailored nanoparticles targeted at therapeutic, diagnostic, agriculture, and food industries.

This book should be immensely useful for plant biologist, microbiologists, nanotechnologists, ecologist, researchers, technocrats, and scientists of biological sciences and those who are interested in recent advancement in food and environmental nanotechnology. I am honored that the leading scientists who have extensive, in-depth experience and expertise in nanotechnology took the time and effort to develop these outstanding chapters. Each chapter is written by internationally recognized researchers/scientists so the reader is given an up-to-date and detailed account of our knowledge of the nanobiotechnology and innumerable applications of nanoparticles.

We are indebted to the many people who helped to bring this book to light. We wish to thank Dr. Mamta Kapila, Senior Editor, Springer; Mr. Joseph Daniel, Project

Coordinator, Springer; and Mr. Balaji Padmanaban, Project Manager, SPi Global, for generous assistance, constant support, and patience in initializing the volume. Dr. Prasad in particular is very thankful to Professor Ajit Varma, Amity University, for the kind support and constant encouragement. Special thanks are due to my esteemed friends, well-wishers, and all faculty colleagues of Amity University.

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About the Editors

Ram Prasad, Ph.D. is assistant professor at the Amity Institute of Microbial Technology, Amity University, Uttar Pradesh, India. His research interest includes plant-microbe interactions, sustainable agriculture, and microbial nanobiotechnology. Dr. Prasad has more than a hundred publications to his credit, including research papers and book chapters and five patents issued or pending, and edited or authored several books. Dr. Prasad has 11 years of teaching experience, and he has been awarded the Young Scientist Award (2007) and Prof. J. S. Datta Munshi Gold Medal (2009) by the International Society for Ecological Communications, the FSAB fellowship (2010) by the Society for Applied Biotechnology, the Outstanding Scientist Award (2015) in the field of microbiology by Venus International Foundation, and the American Cancer Society UICC International Fellowship for Beginning Investigators (USA, 2014). In 2014–2015, Dr. Prasad served as visiting assistant professor in the Department of Mechanical Engineering at Johns Hopkins University, USA.

Manoj Kumar, Ph.D. is a scientist with sanguine behavior who adores about research and development, with a commitment to lifelong learning. He is determined on high-quality science that contributes broadly to increasing intellectual knowledge of both plant development and the ecological niche. He has a high level of professional desire for intellectual pursuits and the potential to fulfill his dream of high-impact publications and future recognition of these by academic peers. Dr. Kumar has pursued his Ph.D. in plant biotechnology from the prestigious Jawaharlal Nehru University and then been awarded two postdoctoral fellowships consecutively: (1) DBT-PDF from the IISc, Bangalore, in 2005 and (2) then NRF-PDF from the University of Pretoria. Dr. Manoj Kumar is a researcher of plant biotechnology in the Division of Microbial Technology at Amity University, Uttar Pradesh, India. He referees for journals, including the *International Journal of Phytoremediation*, the *Journal of Soils and Sediments*, and many more. Dr. Kumar's research is on the integration of microbial genetics with a breadth of plant physiological approaches to enable novel gene discovery and conferring metabolites.

Vivek Kumar, Ph.D. is a scientist involved in teaching, research, and guidance, with a pledge to enduring knowledge. Dr. Kumar works at the Amity Institute of Microbial Technology at Amity University Uttar Pradesh, Noida, India. He obtained his master's and doctoral degree from CCS Haryana Agricultural University, Hisar, Haryana, India. He serves on the editorial board of reputed international journals, He has published 63 research papers, 30 book chapters, 6 review articles, and 7 books. Dr. Kumar has also served as microbiologist for 8 years in the Department of Soil and Water Research, Public Authority of Agricultural Affairs & Fish Resources, Kuwait. Dr. Kumar has organized a number of conferences/workshops as convener/organizing secretary. Dr. Kumar's research areas are plant-microbe interactions, environmental microbiology, and bioremediation. He has been credited with first time reporting and identification of pink rot inflorescence disease of date palm in Kuwait caused by Serratia marcescens. He received the "Young Scientist Award" for the year 2002 in "agricultural microbiology" by the Association of Microbiologists of India (AMI).

Dr. Kumar is establishing an "unearthing and deliverance system," where a balance is being strived between development of drought- and salinity-resistant microbiome for better crop production in rain-fed and saline areas.

Production of Cellulose Nanofibrils and Their Application to Food: A Review

1

Hansol Lee, Jaya Sundaram, and Sudhagar Mani

Abstract

Cellulose nanofibrils (CNFs) are one type of nanostructured cellulosic materials with a width below 100 nm and a length of several micrometers. CNFs have many desirable characteristics, such as a unique rheological behavior, high mechanical and barrier properties, and lightweight. They are produced from cotton, wood, grasses, and other lignocellulosic biomass. Thus, CNFs are abundantly available and can be a cheap alternative to petroleum-based polymers. Manufacturing of CNFs consists of pretreatment process and mechanical disintegration process. The pretreatment process makes cellulose fibers more responsive to be fibrillated, and pretreated fibers are mechanically disintegrated into nano-sized fibers in the next stage. Moreover, the type of raw materials can be a principal factor that affects CNFs production and properties. In this chapter, we reviewed the production, characterization, and the current applications of nanocellulose for food industries, such as food additives, food packaging, and coating.

Keywords

Cellulose nanofibrils • Nanocellulose • Food applications • Food additives • Food packaging • Food coating

1.1 Introduction

Cellulose is the most abundant natural biopolymer derived from wood, cotton, and other non-wood fiber sources (agricultural residues and grasses). Paper and pulp industries are converting woody biomass into various formats of cellulose fibers for

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manufacturing papers, tissues, moisture absorbents, and several cellulose derivatives for chemical and pharmaceutical applications. For example, ethyl cellulose is commercially used in coating, binding, and controlled-release drug systems. Other ether derivatives, such as carboxymethyl cellulose and hydroxyethylcellulose, are also used as a viscosity modifier, a gelling agent, a foaming agent, and a binding agent (Dufresne 2012).

Cellulose nanofibrils (CNFs) are one type of nanostructured cellulose, which has a width of below 100 nm and a length of several micrometers. CNFs were first produced by Turbak et al. (1983a) and Herrick et al. (1983). Cellulose nanofibrils have many advantages over ordinary cellulose fibers since CNFs are much lighter but have more extensive network structures, resulting in higher mechanical and barrier properties. CNFs film has a tensile strength as high as 310 MPa and an oxygen permeability as low as 0.00006 cc.μm/m^2.day.kPa, which are competitive with those of other commercial polymers (up to 70 MPa) (Stevens 1999; Saito et al. 2009; Nair et al. 2014). CNFs also have unique rheological properties. They have a high viscosity with shear-thinning behavior. The unique properties of CNFs have been studied in the broad range of applications such as food, cosmetic, electronic, and biomedical applications. Specifically, CNFs have been used in many different ways to food products, such as food additives, food packaging, and coating films.

CNFs are produced by disintegrating cellulose fibers using mechanical methods, such as high-pressure homogenization, micro-fluidization, and micro-grinding. The mechanical disintegration methods consume high energy and pose clogging issues to successfully produce CNFs. Cellulose fibers are pretreated using mechanical, chemical, and/or enzymatic methods to make the fibers more susceptible to disintegration. The selection of raw materials also affects the ease of CNFs production. The disintegration of hardwood cellulose fibers is more difficult than that of softwood cellulose fibers due to the rigidity and complexity of hardwood cell wall (Stelte and Sanadi et al. 2009). Compared with cellulose fibers from wood, cellulose fibers from non-woody plants might be more favorable to produce cellulose nanofibrils because non-woody plant fibers are present in thin primary cell walls.

This paper first aims to investigate the effects of raw materials on the production and properties of cellulose nanofibrils. Several review articles on cellulose nanofibrils produced from either cotton/wood sources or bacterial source have been published in the literature (Siqueira et al. 2010; Siro and Plackett 2010; Lavoine et al. 2012; Abdul Khalil et al. 2014; Jonoobi et al. 2015) with limited focus on the interaction effects of preparation methods and raw materials on CNFs production and their application to food. Also, since cellulose nanofibrils have a number of potential applications, reviews of nanocellulose applications in the fields of papermaking (Brodin et al. 2014; Osong et al. 2016), biomedical engineering (Lin and Dufresne 2014; Lu et al. 2014; Jorfi and Foster 2015; Guise and Fangueiro 2016), and electronics (Kim et al. 2015; Hoeng et al. 2016; Sabo et al. 2016) were found in the literature. The use of CNFs in food science has been recently summarized (Gómez et al. 2016).

This chapter reviews a wide range of CNFs applications to food industries, including food additives, food packaging and edible film/coating applications.

1.2 Cellulose and Nanocellulose

1.2.1 Cellulose

Cellulose is the most abundant natural polymer as it is the main component of plant cell walls. It is an almost inexhaustible source as the estimated annual biomass production is approximately 1.5 × 10^{12} tons in the US. Cellulose is a linear polymer of the repeating units of β-D-glucopyranose which are linked by linear β-1,4 glucosidic linkages (Fig. 1.1). Cellulose has a large number of hydrogen groups at C-2, C-3, and C-6 atoms. Due to its linear structure and multiple hydroxyl groups, cellulose can form extensive intra- and intermolecular hydrogen bonds, which enables cellulose to form a stable three-dimensional structure. Intramolecular hydrogen bonds are also responsible for cellulose stiffness and its insolubility in most solvents (Gavillon 2007; Wang 2008). Besides, cellulose has a hierarchical morphological structure: elementary fibrils (1.5–3.5 nm in widths), microfibrils (10–30 nm in widths), and microfibril bands (larger than 100 nm in widths) (Klemm et al. 2005). The elementary fibrils pack to the microfibrils, and the microfibrils form the core structural units of the plant cell wall. Each microfibril can be realized as a string of cellulose crystals, linked along the chain axis by disordered amorphous regions, merging into fibril bundles.

Cellulose is a skeletal component in plants that has ordered cell wall layers. Figure 1.2 schematically represents the cell wall of wood fibers. In most plant fibers, cellulose predominately exists in the central layer (S2) of a secondary cell wall, and it is surrounded by the amorphous matrix substances (hemicellulose and lignin, Fig. 1.3). The distribution of cellulose, hemicellulose, and lignin differs depending on the plant type. For instance, softwood typically has 42%, 27%, and 28% of cellulose, hemicellulose, and lignin content, respectively, while hardwood has 45%, 30%, and 20%, respectively (Smook 2002).

1.2.2 Nanocellulose

Nanocellulose refers to a cellulosic nanomaterial that has at least one dimension on a nanoscale. It can be classified into three types, cellulose nanofibrils (CNFs), cellulose nanocrystals (CNCs), and bacterial nanocellulose (BNC), adapted from

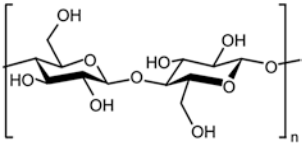

Fig. 1.1 Chemical structure of cellulose

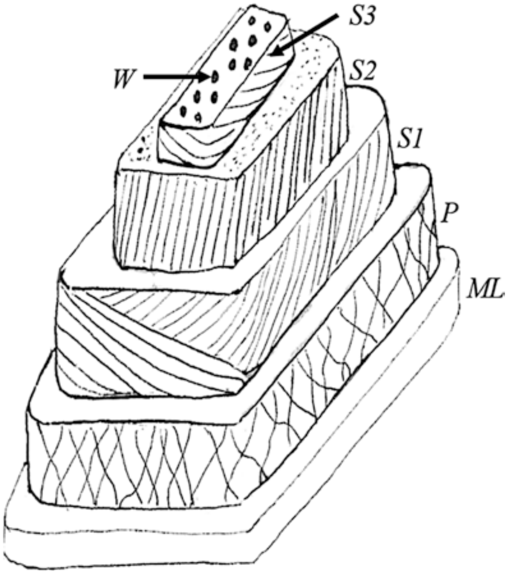

Fig. 1.2 Schematic structure of wood fiber: *ML* middle lamella, *P* primary cell wall layer, *R* reversing point, *S1* outer layer of secondary cell wall, *S2* middle layer of secondary cell wall layer 2, *S3* inner layer of secondary cell wall, *W* wart layer (Modified from Krässig 1993)

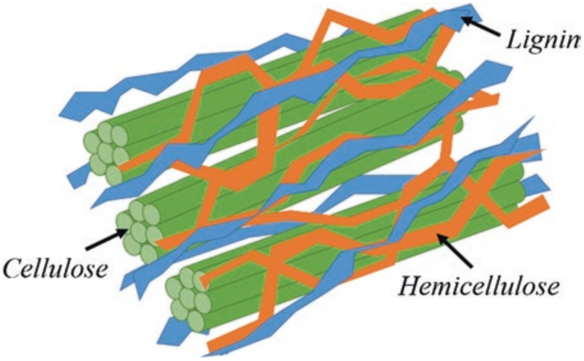

Fig. 1.3 Cellulose fibrils surrounded by hemicellulose and lignin

Klemm et al. (2011). Each type of nanocellulose is obtained using different preparation methods. The production of CNFs and CNCs is the top-down process, where lignocellulosic materials are broken down into microscale cellulosic materials and further disintegrated into nanocellulose materials (Fig. 1.4). On the other hand, bacterial cellulose production is a bottom-up process where bacteria generate glucose and cellulose is synthesized by connecting glucose molecules. Each nanocellulose type has a different dimension that affects its functions. CNFs and CNCs can be produced from lignocellulosic materials as shown in Fig. 1.5.

First, cellulose nanofibrils, known as microfibrillated cellulose, nanofibrillated cellulose, and cellulose nanofibers, were first developed by Turbak et al. (1983a) and Herrick et al. (1983). They conducted mechanical refining and a high-pressure homogenization processes with wood cellulose fibers, and they obtained a gel-like

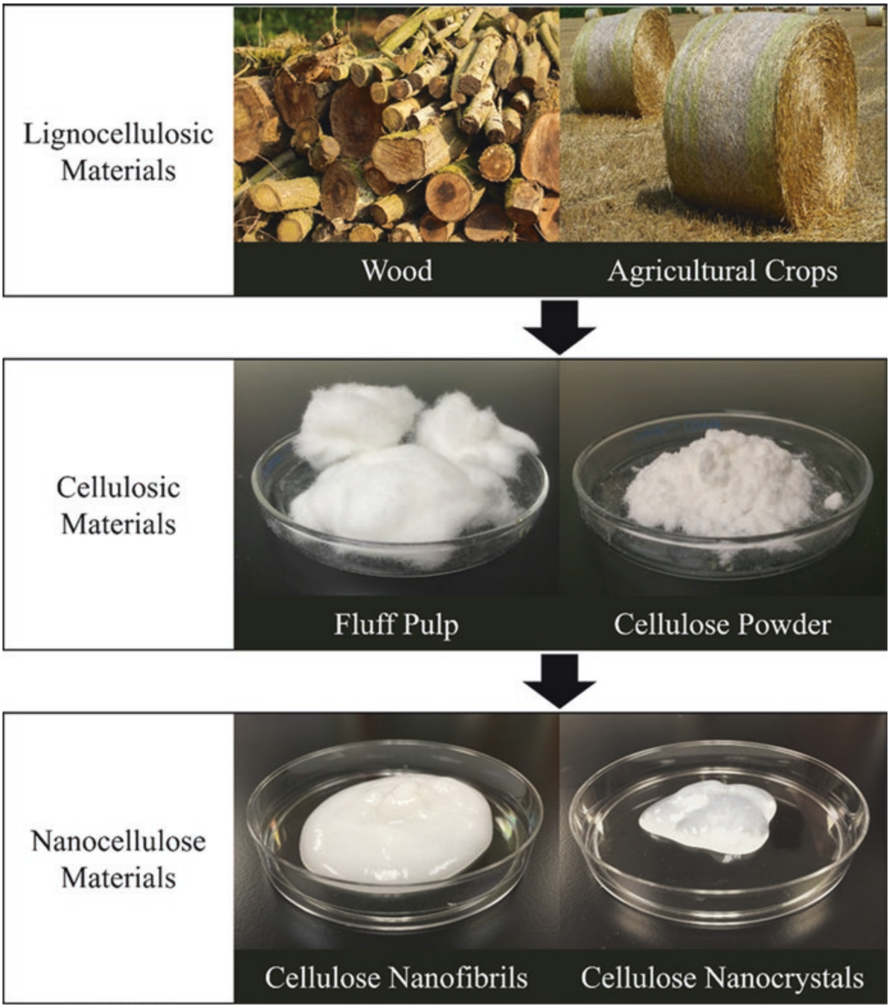

Fig. 1.4 From lignocellulosic materials to nanocellulose materials

material, naming this new material as microfibrillated cellulose. Since then, a number of studies have been conducted on cellulose nanofibrils. Cellulose nanofibrils typically have a diameter of below 100 nm and a length of several micrometers (Klemm et al. 2011). Due to high aspect ratio (length/width), they form rigid network structures that induce remarkable mechanical and barrier properties. It has been reported that the CNFs films have a tensile strength of up to 310 MPa, which is much higher than commercial polymers, such as polyethylene, polystyrene, and polycarbonate (up to 70 MPa) and high performance polymers, such as polyimide and polyetheretherketon (70–100 MPa) (Stevens 1999; Yano and Nakahara 2004; Abe and Yano 2009; Fukuzumi et al. 2009; Saito et al. 2009). CNFs have been

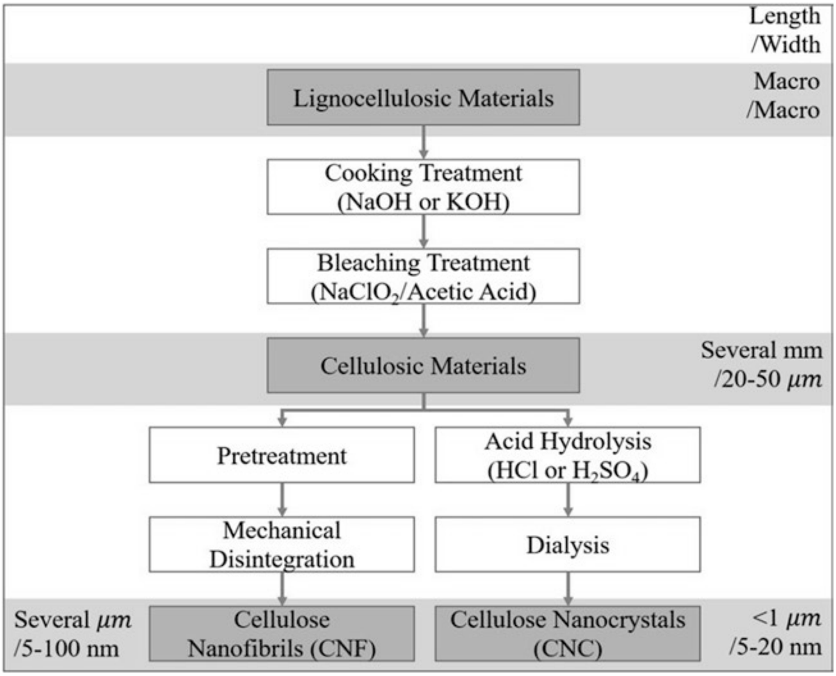

Fig. 1.5 A brief production process of cellulose nanofibrils (*CNFs*) and cellulose nanocrystals (*CNCs*) from lignocellulosic materials

incorporated as a reinforcing agent into various polymer matrices, such as polypropylene, poly(lactic acid), and starch. For instance, Fernandes et al. (2010) reported that chitosan/CNFs nanocomposite films had up to threefold higher Young's modulus compared with pure chitosan at 60% CNFs loading. CNFs films also have excellent barrier performance. Aulin et al. (2010) described the oxygen permeability of CNFs films at 0% RH was 0.0006 cm^3.μm/m^2.day.kPa, which is much lower than that of polyethylene and polystyrene. Also, CNFs gels have not only high viscosity but also a high degree of shear thinning, which make them injectable as well as moldable for a number of biomedical and food applications (Pääkkö et al. 2007).

Mechanical disintegration process is required to obtain well-delaminated cellulose nanofibrils from cellulose fibers, which are held by hydrogen bonds. The equipment commonly used to produce CNFs includes a high-pressure homogenizer, a micro-fluidizer, and a micro-grinder. However, there are several technical problems in the mechanical disintegration process, such as high energy consumption and clogging in a homogenizer (Klemm et al. 2011). More specifically, the energy required by a high-pressure homogenizer reaches as high as 70,000 kWh/ton (Eriksen et al. 2008). By comparison, the average US household consumed 11,320 kWh of electricity in 2009 (EIA 2009). Despite this high energy demand, the research on CNFs has become a rapidly evolving research area because of the increasing demand for renewable materials and interest in nanotechnology since 2000. Researchers have developed mechanical, chemical, and/or enzymatic pretreatment methods that make large-scale CNFs production available since the pretreatment facilitates the fibrillation process, reducing energy consumption and clogging. Several pilot and commercial plants for cellulose nanofibrils have opened since 2011.

Cellulose nanocrystals, called nanocrystalline cellulose, cellulose whiskers, and cellulose nanowhiskers, consist of rodlike cellulose particles. CNCs have a width ranging from 5 to 60 nm, and length varies to several nanometers depending on the sources of cellulose. For instance, CNCs obtained from plants have a length of 100–250 nm, while CNCs from tunicate, algae, and bacterial celluloses have a length from 100 nm to several micrometers. CNCs are prepared by strong acid hydrolysis, often followed by sonication. During the acid hydrolysis, amorphous regions of cellulose fibers are removed as the hydronium ions attack weak points of cellulose (glucosidic bonds in amorphous regions); thus, cellulose nanocrystals are highly crystalline (Siqueira et al. 2010). Hydrochloric and sulfuric acids are the two most used acids for CNCs extraction. Sulfuric acid is more commonly used as it reacts with the hydroxyl groups of cellulose, rendering the negatively charged surface sulfate groups. The charged groups create the repulsive forces between cellulose, which allow CNCs homogeneously dispersed in water (Dong et al. 1998). CNCs can be used as a reinforcing agent in polymer composites, but they create a weak reinforcing effect compared with CNFs because of their lower aspect ratio (Xu et al. 2013).

Bacterial nanocellulose (BNC) is generated by *Gluconacetobacter* bacteria strains. BNC is produced by a biotechnological bottom-up method unlike CNFs and CNCs. It is synthesized from biochemically activated dextrose between the outer and plasma membranes of the bacterial cell by a cellulose-synthesizing complex. This complex is associated with pores at the surfaces of the bacterial cell, having a diameter of about 3 nm (Gatenholm and Klemm 2010). BNC has a width ranging from 20 to 100 nm (Klemm et al. 2011). It has extensive networks due to the random motion of bacteria. Moreover, BNC is pure cellulose that does not include functional groups, such as carbonyl and carboxyl groups, and other polymers, such as hemicellulose and lignin; therefore, it is the most used nanocellulose in the biomedical application (Gatenholm and Klemm 2010).

1.3 Production of Cellulose Nanofibrils

Cellulose nanofibrils are typically prepared by mechanical disintegration process using three common methods: high-pressure homogenization (Herrick et al. 1983; Turbak et al. 1983a, b; Dufresne et al. 2000; Iwamoto et al. 2005; Malainine et al. 2005; Besbes et al. 2011a, b; Li et al. 2012; Alila et al. 2013; Chaker et al. 2013), micro-fluidization (Pääkkö et al. 2007; Zimmermann et al. 2010; Spence et al. 2011; Zhu et al. 2011; Zhang et al. 2012), and micro-grinding (Iwamoto et al. 2005, 2007, 2008; Jonoobi et al. 2012; Josset et al. 2014; Sharma et al. 2015). Each method has its advantages and disadvantages.

High-pressure homogenization is the first method used to produce cellulose nanofibrils from woody cellulose fibers (Herrick et al. 1983; Turbak et al. 1983a).

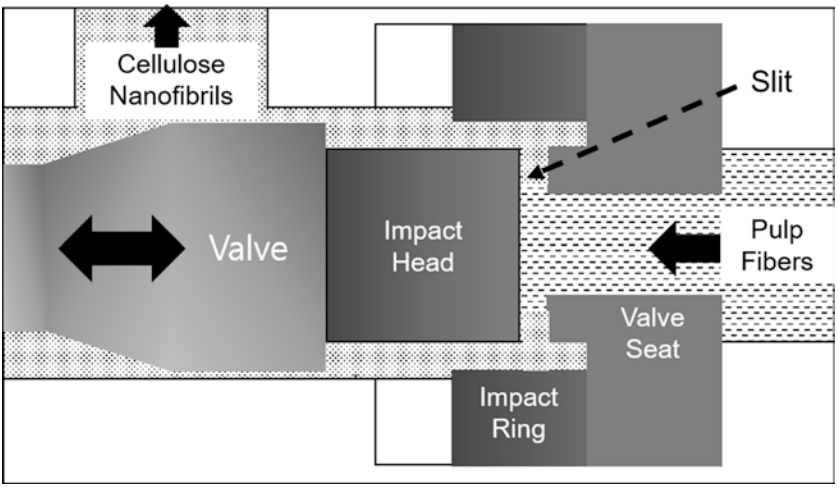

Fig. 1.6 Description of homogenizer systems

Cellulose aqueous suspension is pumped at high pressure through a spring-loaded valve assembly. The valve is opened and closed repetitively, so the fibers are subjected to a significant pressure drop with high shear and impact forces generated in the narrow slit of the valve and disintegrated into cellulose nanofibrils (Fig. 1.6). The process can be easily scaled up and operated continually. However, it consumes a substantial amount of energy over 25,000 kWh/ton and causes clogging in the homogenizer, particularly at the in-line valves, which must be dissembled and cleaned. A micro-fluidizer is an alternative to the high-pressure homogenizer. The cellulose/water slurry is passed through thin z-shaped chambers with different channel dimensions (commonly 100–400 μm) under high pressure (Fig. 1.7). Then, it is converted into a gel-like material by the application of shear and impact forces. This process does not use in-line moving parts, thus reduces the likelihood of clog. If the clogging occurs, the micro-fluidizer has to be cleaned by reverse flow through the chamber.

When processing with a micro-grinder, cellulose/water suspension is passed between a static and a rotating grindstone generally at 1500 rpm. Cell wall structures and hydrogen bonds are broken down by the shearing forces generated by the grinding stones, and nanofibers in a multilayer structure are liberated. This method is considered less energy demanding than the other two methods, and it does not have issues related to clogging. However, the main disadvantage of micro-grinding is disk maintenance and replacement due to frequent worn out.

Ultrasonication is an alternative method to produce cellulose nanofibrils (Chen et al. 2011a, b). Ultrasound energy is transferred to cellulose chains through a cavitation process where cavities in water are formed, grow, and are violently disrupted. The energy generated by cavitation is roughly 10–100 kJ per mol that is within the hydrogen bond energy scale. Therefore, the ultrasonic impact can break down hydrogen bonds and disintegrate cellulose fibers into cellulose nanofibrils. However,

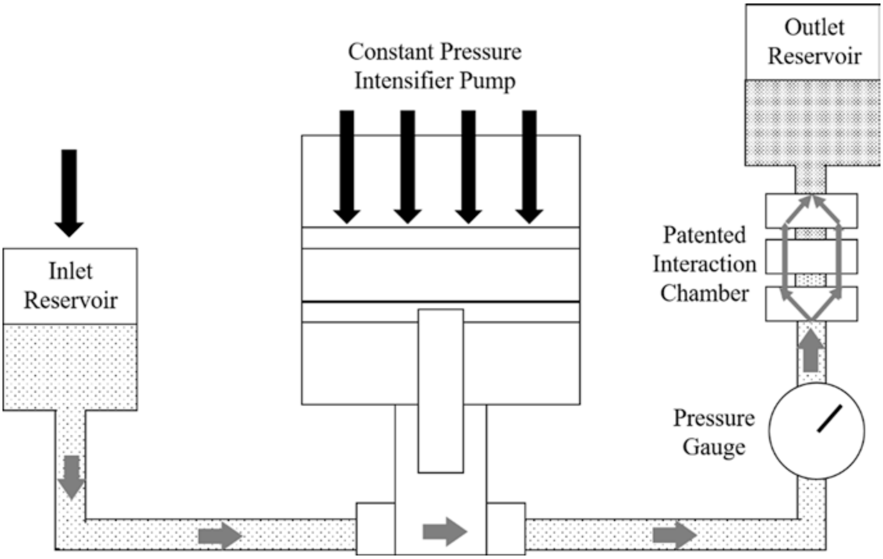

Fig. 1.7 Description of micro-fluidizer systems

the multilayered cell wall structure and interfibrillar hydrogen bonds inhibit the complete fibrillation of cellulose fibers into individual microfibrils; thus CNFs are usually obtained as aggregates of microfibrils having a wide distribution in width (Chen et al. 2011a). For this reason, high output energy of ultrasonication is required to obtain well-fibrillated cellulose. When the output power of ultrasonication was 1000 W or higher, CNFs had a narrow distribution in width (5–20 nm) with a web-like network structure; on the other hand, 400 W ultrasonic treatment produced large aggregates of cellulose fibers with widths ranging from several nanometers to a hundred nanometers.

A high-speed blender has been recently introduced to prepare cellulose nanofibrils (Uetani and Yano 2011; Jiang and Hsieh 2013). Uetani and Yano (2011) produced cellulose nanofibers by agitating 0.7 wt.% pulp/water slurry using a blender at 37,000 rpm for 30 min. The resultant cellulose nanofibrils had a uniform width of 15–20 nm. They reported that high-speed blending process could yield the same extent of fibrillation of cellulose with less damage on CNFs compared with micro-grinding. Jiang and Hsieh (2013) also prepared CNFs using high-speed blending, and the CNFs exhibited superior crystallinity (81.5%) compared with original rice straw cellulose (72.2%), confirming high-speed blending did not cause severe damage on cellulose. Interestingly, these CNFs had a bimodal distribution of dimensions: an average width of 2.70 nm or 8.46 nm and a length of 100–200 nm or several micrometers.

1.4 Pretreatment Methods for CNFs production

1.4.1 Mechanical Pretreatments

Mechanical pretreatment methods aim to pre-fibrillate cellulose fibers and reduce fiber size to facilitate the fiber disintegration easily. They can damage the cellulose fibrillary structure, causing external fibrillation that exposes secondary cell wall, where individual cellulose fibrils are organized. They can also produce internal fibrillation that loosens the fiber wall (Hamad 1997; Nakagaito and Yano 2004). Alternatives to mechanical pretreatment include manual cutting, disk refiners, PFI mills, Valley beaters, and blenders (Herrick et al. 1983; Turbak et al. 1983a; Dinand et al. 1999; Dufresne et al. 2000; Chakraborty et al. 2005; Iwamoto et al. 2005; Malainine et al. 2005; Spence et al. 2011; Zhang et al. 2012). The PFI mill and the Valley beater are commonly used for refining pulps in the laboratory scale. Firstly, the PFI mill is a high-energy and low-intensity refiner (Gharehkhani et al. 2015). This device refines pulps between the inner roll and outer bedplate that rotate in the same direction but with different peripheral speeds; thus, the pulps are exposed to mechanical shearing action (TAPPI 2000). The Valley beater needs the larger amount of pulp samples and longer operating time (Gharehkhani et al. 2015). In the beating process, the pulps are looped around a well and forced between a rotor and loaded bedplate (TAPPI 2001). The energy consumption of PFI mill and Valley beater led to increased cost of manufacturing cellulose nanofibrils. It was reported that the effective beating energy in a Valley beater was about 482 and 578 kWh/ton for bleached eucalyptus and bleached pine, respectively, for a total beating time of 1 h. When no-load power was included, the total beating energy was approximately 3000 kWh/ton (Atic et al. 2005). It was also reported that the 3-h beating process consumed about 2000 kWh/ton while producing cellulose microfiber 0.24 μm in diameter from cellulose fibers 30 μm in diameter (Spence et al. 2011). Concerning the PFI mill, Welch and Kerekes (1994) estimated the refining energy for PFI milling was about 0.18 kWh/ton-rev. If the pulps are refined in a PFI mill for 20,000 revolutions prior to the mechanical disintegration process as described by Sharma et al. (2015), the PFI mill would consume approximately 3600 kWh/ton. Also, the refining energy required by a PFI mill was estimated as high as 21,700 kWh/ton to generate cellulose microfiber 1.3 μm in diameter from bleached softwood kraft pulp 13 μm in diameter (Chakraborty et al. 2007b). Therefore, the development of low-energy mechanical pretreatment technique can contribute to the reduction in the overall energy use for CNFs production. Moreover, the standard mechanical refining process is a wet processing. The mechanical pretreatment process using a PFI mill is performed at the initial pulp consistency of 10%. Specifically, 300 g of cellulose slurry containing 30 g of cellulose (dry basis) can be refined per run (TAPPI 2000). The process with a Valley beater is carried out at the pulp consistency of 1.57%, having 360 g of cellulose (dry basis) in 23 L (TAPPI 2001). This indicates that both mechanical pretreatment processes produce wet cellulose precursors, and their bulk volume would make it difficult to store and handle these cellulose precursors.

1.4.2 Chemical Pretreatments

Several chemical pretreatments have been developed to facilitate the mechanical disintegration of cellulose. 2,2,6,6,-tetramethylpiperidine-1-oxyl radial (TEMPO)-mediated oxidation has been widely studied as a chemical pretreatment for cellulose nanofibrils production (Alila et al. 2013; Besbes et al. 2011a, b; Chaker et al. 2013; Saito et al. 2006, 2007; Zhang et al. 2012). This process converts half of C6 primary hydroxyl groups on a cellulose surface into C6 carboxyl groups (Fig. 1.8). TEMPO oxidation helps cellulose fibers to be delaminated in several ways: (1) repulsive forces between cellulose fibers form the introduction of the carboxyl groups; (2) TEMPO oxidation favors the hydration and swelling of cellulose fibers, making the fibers more flexible and also increasing the accessibility of their crystalline regions; (3) the oxidation also makes the S2 layer more accessible and more prone to be fibrillated by loosening the primary S1 cell wall; and (4) the oxidation leads to chain scission in the amorphous region, which creates weak points within the cell wall (Besbes et al. 2011a).

Carboxymethylation process is another common chemical pretreatment method. Cellulose fibers are first reacted with sodium hydroxide to become more accessible to chemicals and then with monochloroacetic acid to introduce carboxymethyl groups as shown in Fig. 1.9. The introduction of charged groups enhanced the delamination of cellulose fibers by giving repulsive electrostatic forces between fibers. Also, carboxymethylation leads to fiber swelling, and carboxymethyl groups should be in the form of their sodium salts in order to cause as much swelling of cellulose fibers as possible. Swollen fibers are more susceptible to be delaminated

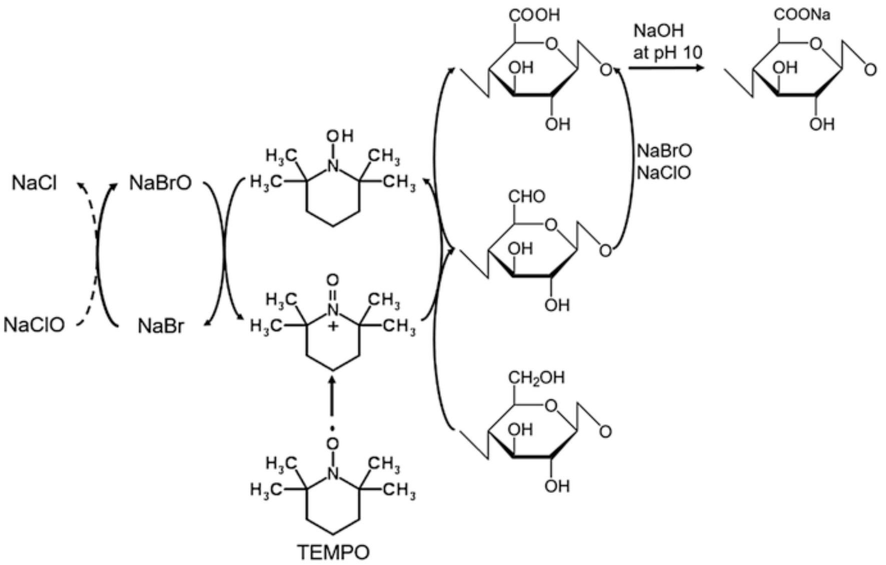

Fig. 1.8 TEMPO-mediated oxidation of cellulose at pH 10–11

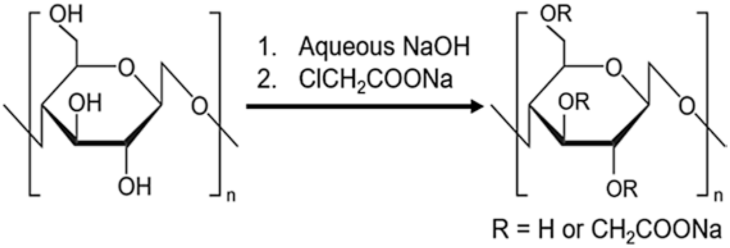

Fig. 1.9 Carboxymethylation of cellulose

as they have lower cell-wall cohesion than less swollen fibers (Klemm et al. 2011). It was reported that with the carboxymethylation process, cellulose nanofibrils were successfully obtained only after one pass through a high-pressure fluidizer and had a diameter of 5–10 nm (Wågberg et al. 2008; Aulin et al. 2010).

There are several disadvantages of chemical pretreatment methods. First, these processes require various chemicals and organic solvents, which is far from environmentally benign technology. TEMPO oxidation uses sodium hypochlorite and/or sodium chlorite, sodium bromide, TEMPO, and ethanol. Carboxymethylation is based on the reaction in organic solvents, such as ethanol, methanol, and isopropanol. More specifically, a total of 30 kg of organic solvents are consumed during carboxymethylation to manufacture 1 kg of cellulose nanofibrils (Arvidsson et al. 2015). In addition, the introduction of functional groups, such as carboxyl and carboxymethyl groups, decreases thermal stability of cellulose due to decarbonation (Britto and Assis 2009). Fukuzumi et al. (2009) demonstrated that TEMPO-oxidized cellulose nanofibrils had an onset thermal degradation temperature (T_o) of approximately 200 °C, while original cellulose had a T_o of approximately 300 °C. Other studies also confirm that the thermal degradation of cellulose nanofibrils containing functional groups takes place at a lower temperature than pure cellulose nanofibrils (Eyholzer et al. 2010; Fukuzumi et al. 2010).

Ionic liquids have been used to promote mechanical disintegration process. Li et al. (2012) studied imidazolium-based ionic liquid treatment to obtain nanocellulose from sugarcane bagasse using a high-pressure homogenization. Before homogenization, cellulose fibers were pretreated with [Bmim]Cl ionic liquid (IL) which attacked and broke the hydrogen bonds between cellulose fibers. IL-treated fibers were passed through a high-pressure homogenizer, and then nanocellulose was generated with a width of 10–20 nm. However, IL treatment has some drawbacks. First, this treatment decreased the crystallinity of cellulose, thereby the thermal stability of cellulose. The crystallinity of original cellulose, IL-treated cellulose, and nanocellulose was 60%, 52%, and 36%, respectively, because the IL treatment and homogenization made cellulose more amorphous, resulting from the destruction of intermolecular hydrogen bonds. The decrease in an onset decomposition temperature is another evidence of the cellulose disruption. The onset decomposition temperature of untreated cellulose was 288 °C, while those of IL-treated cellulose and nanocellulose were 251 °C and 238 °C, respectively. Furthermore, imidazolium-based ionic liquid is expensive and non-environmentally friendly because the feedstock for the synthesis of the ionic liquid is of petroleum based (Hou et al. 2012).

1.4.3 Enzymatic Pretreatment

Enzymatic pretreatment has been used as an environmentally benign pretreatment for cellulose nanofibrils production, which is based on hydrolysis of cellulose, in particular, glucosidic bonds in amorphous regions (Zhu et al. 2011). Cellulases used for enzymatic pretreatment can be divided into two categories as follows (Dufresne 2012): (1) endoglucanases or β-1,4-endoglucanases, which randomly attack intramolecular β-1,4-glucosidic bonds, creating oligosaccharides of various lengths and hence new chain ends, and (2) exoglucanases or cellobiohydrolases, which act on the chain ends, generating cellobiose or glucose. The selection of cellulases used affects the type of nanocellulose obtained. Siqueira et al. (2010) pretreated sisal fibers with two types of cellulases, an endoglucanase and an exoglucanase. The enzymatic treatment was performed before (as pretreatment) or after (as posttreatment) mechanical disintegration process with a micro-fluidizer. It was reported that regardless of the order of the enzymatic treatment conducted (pre- or posttreatment), the use of endoglucanases produced a mixture of CNFs and rodlike nanoparticles, while CNFs with network structures was obtained with the exoglucanases used.

Pääkkö et al. (2007) attempted to obtain CNFs using a high-pressure homogenizer with or without mild enzymatic pretreatment using endoglucanases. They found that the use of untreated cellulose fibers caused the rapid blocking of the homogenizer and needed an enormous amount of energy to produce cellulose nanofibrils. A large portion of non-fibrillated cellulose was observed. In contrast, when enzymatically pretreated cellulose fibers were used, the homogenization was performed without clogging and with lower energy consumption of approximately 1100 kWh/ton. The resultant CNFs consisted of individual microfibrils with a width of 5 nm and microfibrils aggregates with a width of 10–20 nm. Also, a very small dosage of an enzyme (0.17 μl per gram of fiber) was sufficient to obtain cellulose nanofibrils; on the other hand, too high dosage (30 μl per gram of fiber) reduced the efficiency of fiber refining and homogenization. Henriksson et al. (2007) reported that cellulose nanofibrils were successfully prepared with low enzyme concentration (0.02%), while their molecular weight and fiber length were maintained.

1.5 Effects of Cellulose Sources on CNFs Production

The first raw material used for manufacturing cellulose nanofibrils was wood pulp (Turbak et al. 1983a; Herrick et al. 1983). Since then, wood pulp has been widely used as a source for CNFs production. More specifically, among 31 CNFs manufacturing plants at a pilot or commercial scale, 22 plants have used wood-based material (18 plants for wood and 4 plants for bleached wood pulp) as a starting material (TAPPI 2015, Fig. 1.10). Wood can be classified into two categories, softwood and hardwood,

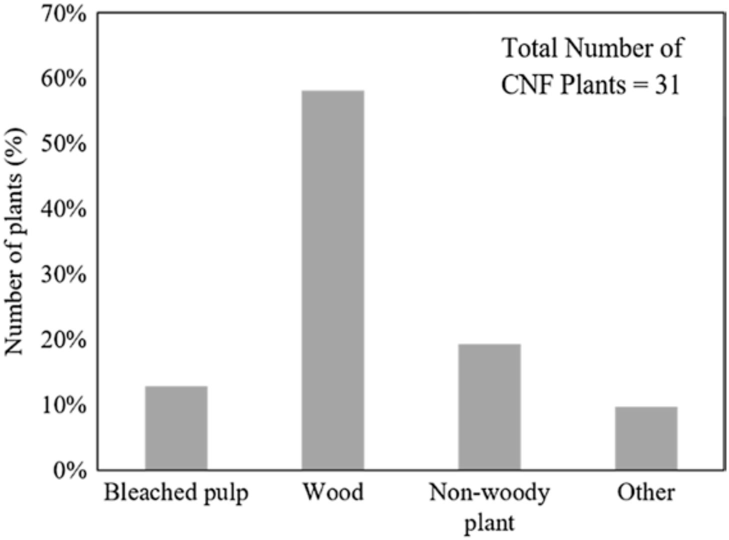

Fig. 1.10 Cellulose sources for CNFs production at pilot or commercial scales

based on the differences in anatomical features. Softwood pulp is the most used raw material for producing CNFs since it is more responsive to be fibrillated even though it typically has higher lignin content compared with hardwood pulp. Hardwood fibers are less flexible than softwood fibers because the outer secondary wall of hardwood fibers is spirally layered, which reduces their flexibility and accessibility to the inner secondary wall (Stelte and Sanadi 2009). Stelte and Sanadi (2009) described that softwood cellulose fibers were fibrillated into aggregates of small fibers after 25 passes through a disk refiner, while hardwood cellulose fibers mostly remained intact after 75 passes. Moreover, the refined softwood fibers were well fibrillated into nanoscale fibers after ten passes through a high-pressure homogenizer, whereas the refined hardwood fibers required 100 passes to be nano-fibrillated.

In addition, softwood is more accessible to be chemically modified, which facilitates cellulose fiber disintegration, compared with hardwood. This is because the dominant component of the softwood hemicellulose is glucomannan which has C6 primary hydroxyl groups that can be converted into other functional groups, such as carboxyl groups. On the other hand, the hardwood hemicellulose is mainly xylan which does not have C6 primary hydroxyl groups (Sjöström 1993; Fukuzumi et al. 2009). Fukuzumi et al. (2009) reported that the light transmittance at 600 nm was 90% for the CNFs film made of TEMPO-oxidized softwood pulp, but it was about 78% for the CNFs film made of TEMPO-oxidized hardwood pulp, indicating that CNFs from softwood was largely nano-fibrillated than those from hardwood.

The demand for wood has been increased since wood is an important material not only for producing pulp but also for other products such as building products, furniture, and energy. For this reason, non-woody plants, such as agricultural crops and by-products, have been studied as a starting material to produce CNFs. In the literature, CNFs have been obtained from various non-woody plants, such as sugar beet pulp (Dinand et al. 1999; Leitner et al. 2007), wheat straw (Alemdar and Sain 2008; Zimmermann et al. 2010), rice straw (Hassan et al. 2012; Jiang and Hsieh 2013), swede root (Bruce et al. 2005), potato tuber (Dufresne et al. 2000), soy hulls (Alemdar and Sain 2008), cladodes (Malainine et al. 2005), sugarcane bagasse (Li et al. 2012), alfalfa (Besbes et al. 2011b; Chaker et al. 2013), sunflower (Chaker et al. 2013), flax, hemp, jute, abaca, and sisal (Alila et al. 2013). Six pilot or commercial CNFs manufacturing plants have used non-woody plants as a starting material for CNFs production.

Non-woody plants have several advantages over wood as a source for CNFs production. First of all, non-woody plants are annually harvested; in other words, the harvest cycle is much shorter compared with wood. Therefore, non-woody plants are considered as a cheaper and more renewable source than wood. These plants also contain a lower amount of lignin than wood (Alila et al. 2013); thus, the processing steps required to separate cellulose fibers from non-woody plants are expected to be fewer than those required with wood. More importantly, non-woody cellulose fibers are extracted from the primary wall, where microfibrils are organized in a loose network; on the other hand, wood cellulose fibers present in the secondary cell wall where microfibrils are tightly packed. Primary cell walls are more fragile with a thickness of 100 nm or less, compared with secondary cell walls with a thickness up to several tens of micrometers (Dinand et al. 1999). Therefore, the delamination of cellulose fibers from non-woody plants might be easier, requiring less energy than from wood.

Cellulose nanofibrils from non-woody plants have comparable characteristics to those of CNFs from wood. Table 1.1 summarizes morphological information of cellulose nanofibrils from different cellulose sources. The type of raw materials does not influence the morphology of the resultant CNFs. Regardless of cellulose sources, CNFs have a width of less than 100 nm and a length of several micrometers. Table 1.2 presents the light transmittance of cellulose nanofibrils suspensions or films. Since non-fibrillated particles scatter light due to the large size, the presence of non-fibrillated particles leads to the reduction in the transparency. In another word, as the degree of fibrillation increases, the light transmittance also increases. There is no significant difference between the light transmittance of CNFs from wood and from non-woody plants. In the literature, the lowest light transmittance value (at 600 nm) was 20% for CNFs films from softwood prepared solely by micro-grinding (Nogi et al. 2009). On the other hand, the highest value was 90% for CNFs film from softwood prepared by TEMPO oxidation and ultrasonication (Fukuzumi et al. 2009) and for CNFs suspension from abaca fibers prepared by TEMPO oxidation and high-pressure homogenization (Alila et al. 2013). In addition, the mechanical properties of CNFs films do not depend on the type of raw materials. The tensile strength of pure CNFs films from wood reaches as high as 310 MPa, while from non-woody plants, as high as 230 MPa. It should be noted that these values are much greater than that of commercial polymers, such as polyethylene, polystyrene, and polycarbonate (up to 70 MPa), and high-performance polymers, such as polyimide and polyetheretherketon (70–100 MPa) (Stevens 1999).

Table 1.1 Morphology of CNFs from different cellulose sources

Cellulose source	Mechanical disintegration technique[a]	Pretreatment technique[b]	Width (nm)	References
Wood				
Softwood	HPH	Mech	10–25	Stelte and Sanadi (2009)
			79	Spence et al. (2010a, b)
			85	Spence et al. (2010a, b)
			265	Spence et al. (2010a, b)
			1006	Spence et al. (2010a, b)
		Mech & Enzm	5–30	Pääkkö et al. (2007)
		TEMPO	5–20	Besbes et al. (2011b)
	MF	Carboxymethylation	5–15	Wågberg et al. (2008)
	MG	None	10–20	Iwamoto et al. (2008)
			20–50	Iwamoto et al. (2007)
			15–20	Uetani and Yano (2011)
			20–90	Taniguchi and Okamura (1998)
	US	None	5–20	Chen et al. (2011a)
			10–20	Chen et al. (2011b)
		Mech & TEMPO	3–4/20–30	Nogi et al. (2009)
	Cryocrushing	Mech	100–1000	Chakraborty et al. (2005)
	Hi-Blend	None	15–20	Uetani and Yano (2011)
Hardwood	HPH	Mech	62	Spence et al. (2010a, b)
			85	Spence et al. (2010a, b)
		TEMPO	5–20	Besbes et al. (2011a, b)
	US	None	10–40	Chen et al. (2011b)
		Mech & TEMPO	3–4/20–30	Nogi et al. (2009)

(continued)

Table 1.1 (continued)

Cellulose source	Mechanical disintegration technique[a]	Pretreatment technique[b]	Width (nm)	References
Non-woody plants				
Alfa	HPH	None	5–80	Chaker et al. (2013)
Opuntia ficus-indica cladodes			>5	Malainine et al. (2005)
Potato tuber			>5	Dufresne et al. (2000)
Sunflower			5–80	Chaker et al. (2013)
Oil palm		Mech	5–40	Jonoobi et al. (2011)
Soy hull		Cryocrushing	20–120	Alemdar and Sain (2008)
Wheat straw			10–80	Alemdar and Sain (2008)
Rice straw		High-shear grinding	3–21	Hassan et al. (2012)
Abaca		TEMPO	20	Alila et al. (2013)
Alfa			5–20	Besbes et al. (2011b)
Flax			30–50	Alila et al. (2013)
Hemp			30–50	Alila et al. (2013)
Jute			30–50	Alila et al. (2013)
Sisal			20	Alila et al. (2013)
Sugarcane bagasse		Ionic liquids	10–20	Li et al. (2012)
Wheat straw	US	None	15–35	Chen et al. (2011b)
Rice straw	Hi-Blend	None	2.7–8.46	Jiang and Hsieh (2013)

[a] *HPH* high-pressure homogenization, *MF* micro-fluidization, *MG* micro-grinding, *Hi-Blend* high-speed blending, *US* ultrasonication

[b] *Mech* mechanical pretreatment, *TEMPO* TEMPO-mediated oxidation, *Enzm* enzymatic pretreatment

Young's modulus of CNFs films from non-woody plants (up to 11 GPa) is also comparable to that of CNFs film from wood (up to 18 GPa) (Table 1.3).

1.6 Cellulose Nanofibrils Applications to Food

Cellulose nanofibrils have numerous desirable properties for food applications (Fig. 1.11). Firstly, CNFs have unique rheological properties. They behave like a gel under normal conditions but flow when shaken or agitated. When the shearing forces are removed, CNFs return to their original state. This rheological behavior allows CNFs to be employed as food additives, such as a thickener, a suspension stabilizer, and a textile modifier. Also, CNFs have a great ability to form transparent

Table 1.2 Light transmittance of CNFs suspensions or films from different cellulose sources

Cellulose source	Mechanical disintegration technique[a]	Pretreatment technique[b]	Film or suspension	Transmittance at 600 nm (%)	References
Wood					
Softwood	HPH	TEMPO	Suspension	75	Besbes et al. (2011b)
	MG	None	Film	20	Nogi et al. (2009)
			Suspension	80	Uetani and Yano (2011)
	Hi-Blend	None	Suspension	78	Uetani and Yano (2011)
	US	TEMPO	Film	90	Fukuzumi et al. (2009)
Hardwood	HPH	TEMPO	Suspension	70	Besbes et al. (2011b)
	MG	None	Film	80	Okahisa et al. (2011)
				33.4	Okahisa et al. (2011)
	US	TEMPO	Film	78	Fukuzumi et al. (2009)
	Stirring	TEMPO	Suspension	30–90	Saito et al. (2007)
Non-woody plants					
Abaca	HPH	TEMPO	Suspension	90	Alila et al. (2013)
Alfa				32	Besbes et al. (2011b)
Flax				40	Alila et al. (2013)
Hemp				32	Alila et al. (2013)
Jute				75	Alila et al. (2013)
Sisal				89	Alila et al. (2013)
Sunflower				75	Chaker et al. (2013)

[a] *HPH* high-pressure homogenization, *MF* micro-fluidization, *MG* micro-grinding, *Hi-Blend* high-speed blending, *US* ultrasonication

[b] *Mech* mechanical pretreatment, *TEMPO* TEMPO-mediated oxidation, *Enzm* enzymatic pretreatment

films due to their nanoscale dimensions and hold outstanding mechanical and barrier properties due to their dense network structure. CNFs have a very high surface area with multiple hydroxyl groups, establishing a good bonding with polymer matrices. Therefore, CNFs films and CNFs-based composites are considered promising for food packaging and coating applications.

Table 1.3 Mechanical properties of CNFs films from different cellulose sources

Cellulose sources	Mechanical disintegration technique[a]	Pretreatment technique[b]	Film preparation	Young's modulus (GPa)	Tensile strength (MPa)	References
Wood						
Softwood	HPH	None	Filtration	15.7–17.5	104–154	Syverud and Stenius (2009)
		Mech	Filtration	16	250	Yano and Nakahara (2004)
			Casting	2.5	80	Stelte and Sanadi (2009)
		Mech & Enzm	Filtration	14	104	Henriksson and Berglund (2007)
	MF	Enzm	Filtration	10.4–13.7	129–214	Henriksson et al. (2008)
		Mech & Enzm	Filtration	0.15–1.0	7.4–23.2	Sehaqui et al. (2011)
		TEMPO	Filtration	1.4–5.0	83.7–120	Sehaqui et al. (2011)
	MG	None	Filtration	11	210	Abe and Yano (2009)
			Filtration	12.8–15.1	213–240	Iwamoto et al. (2008)
	US	TEMPO	Casting	4.4–5.4	7–90	Rodionova et al. (2012)
	Hi-Blend	TEMPO	Filtration	6.9	233	Fukuzumi et al. (2009)
Hardwood	HPH	Mech	Casting	1–3	10–60	Stelte and Sanadi (2009)
	MG	None	Filtration	11	200	Abe and Yano (2010)
	Hi-Blend	TEMPO	Filtration	6.2–6.5	222–312	Saito et al. (2009)
Non-woody plants						
Sugar beet	HPH	Mech	Casting	9.3	104	Leitner et al. (2007)
Rice straw		High-shear grinding	Filtration	4.8	85.7	Hassan et al. (2012)
Potato tuber	MG	None	Filtration	11.4	230	Abe and Yano (2009)
Rice straw				11	230	Abe and Yano (2009)

[a] *HPH* high-pressure homogenization, *MF* micro-fluidization, *MG* micro-grinding, *Hi-Blend* high-speed blending, *US* ultrasonication

[b] *Mech* mechanical pretreatment, *TEMPO* TEMPO-mediated oxidation, *Enzm* enzymatic pretreatment

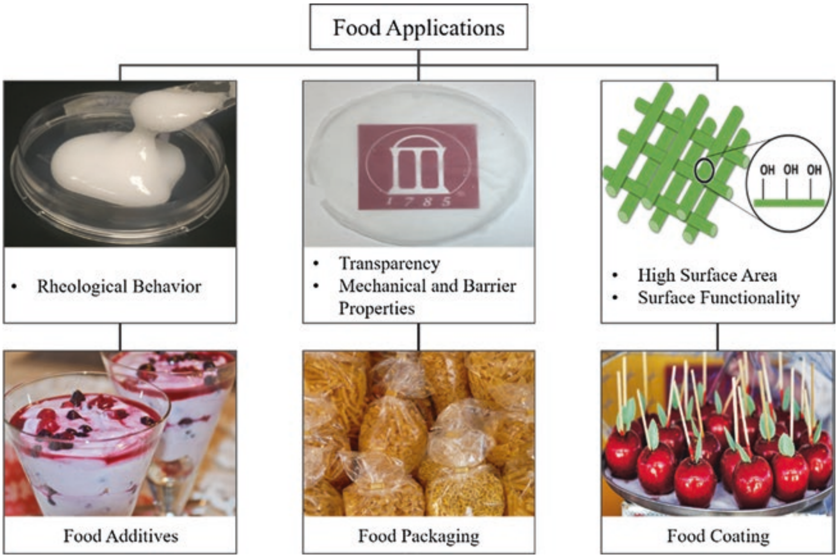

Fig. 1.11 Cellulose nanofibrils food applications

1.6.1 Food Additives

Cellulose nanofibrils in food applications were explored in the early 1980s. CNFs are a gel-like material having pseudoplastic or thixotropic viscosity properties. Therefore, CNFs can be used as various food additives. First, they can be used as an emulsion stabilizer. Turbak et al. (1983b) reported that adding a small amount of CNFs stabilized oil-in-water (o/w) emulsions; for instance, dressing mixtures containing CNFs yielded a stable suspension, showing the uniform distribution through the mix; thus, the mixtures did not require shaking before use. Other studies have also confirmed that CNFs are a useful stabilizer for o/w emulsions (Andresen and Stenius 2007; Xhanari et al. 2011; Ström et al. 2013; Winuprasith and Suphantharika 2013). Winuprasith and Suphantharika (2013) described that cellulose nanofibrils obtained at the higher number of homogenization passes (20 passes) could stabilize o/w emulsions more efficiently, improving the shelf life of the products and making them more aesthetically attractive, compared with CNFs obtained by zero, one, and five homogenization passes (Fig. 1.12). This is because the higher the number of passes, the denser network structures were formed, which are more effective to trap the emulsion droplets, thereby preventing the coalescence of these droplets. Cellulose nanofibrils can be also used as a moisture retention agent in food. Turbak et al. (1983b) reported that meat emulsion containing CNFs formed less fat globules. The hamburgers with CNFs lost less water during frying, which made the hamburgers juicier and tastier compared with those without CNFs. This is in agreement with Ström et al. (2013). They found that CNFs held more water without side effect as watery taste. Moreover, cellulose nanofibrils can be applied as a textile modifier.

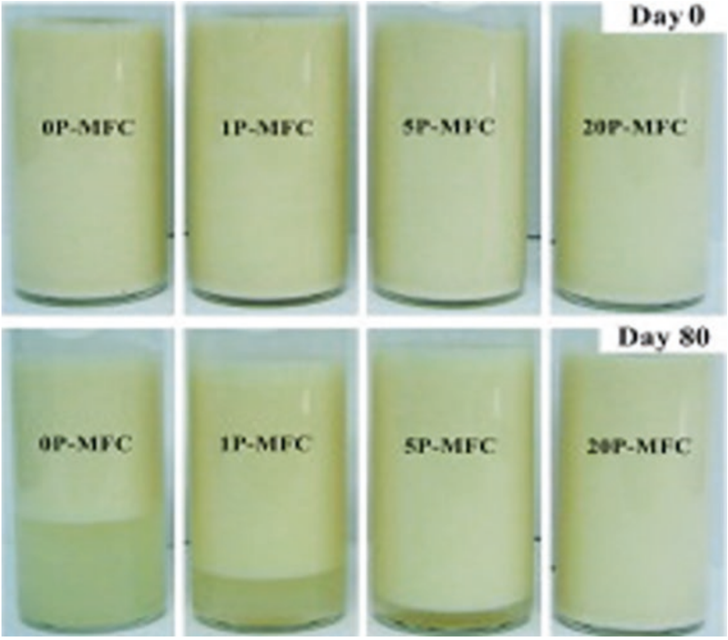

Fig. 1.12 Oil-in-water emulsions (30% w/w oil) stabilized by CNFs prepared with different number of passes through a homogenizer (0, 1, 5, and 20 passes, from left to right, Winuprasith and Suphantharika 2013)

Kleinschmidt et al. (1988) described filling-containing, dough-based products containing cellulose fibrils and microfibrils. They described that cellulose fibrils and microfibrils formed a network, acting as a flow control agent that enabled the filling to be co-based, with the dough forming the crumb. After baking, the filling dispersed rapidly in the mouth, leading to a good eating quality and flavor release. Ström et al. (2013) also reported that bread containing CNFs was softer and had better appearance like higher volume and more even form (Fig. 1.13). Lastly, the addition of cellulose nanofibrils can thicken food products, such as gravies and soups. It was reported that the addition of 0.75% CNFs suspension was sufficient to produce creamed soups (Turbak et al. 1982). It should be noted that since cellulose is not digestible, the use of CNFs in food products does not increase or can reduce calories of the food products (Turbak et al. 1983b).

1.6.2 Food Packaging

CNFs-based materials have proved to be a promising material for food packaging because the addition of cellulose nanofibrils improves mechanical and barrier properties as well as biodegradability. CNFs-based composites have been fabricated with various polymer materials, including hydrophobic polymers, such as polyethylene

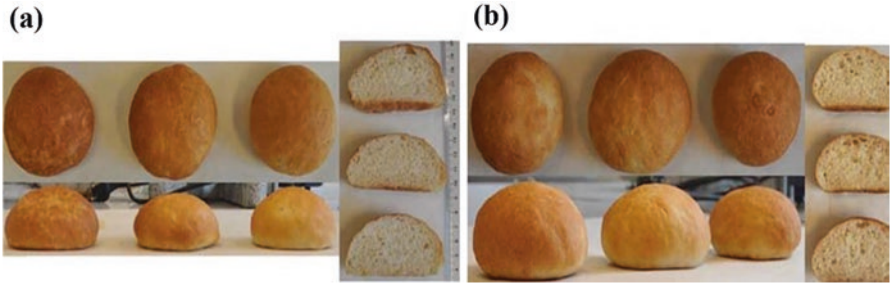

Fig. 1.13 Buns baked from fresh dough with (**a**) no additives and (**b**) cellulose nanofibrils (Reprinted with permission from Innventia AB. Ström et al. 2013)

(PE), polypropylene (PP), and polylactic acid (PLA), and hydrophilic polymers, such as starch, amylopectin, and polyvinyl alcohol (PVA). Moreover, CNFs/Ag composites have been recently developed and can be used as an antimicrobial food packaging film.

1.6.2.1 CNFs/PE and CNFs/PP Composites

It has been attempted to prepare CNFs-based composites with polyethylene (PE) and polypropylene (PP), which are the two most widely used polymers in food packaging industries (Cheng et al. 2007; Wang and Sain 2007a, b). It has been found that the addition of cellulose nanofibrils improves the mechanical and thermal properties of PE and PP composites with an increasing potential of biodegradability. Cheng et al. (2007) fabricated CNFs/polypropylene composites and reported that the tensile strength and Young's modulus of CNFs/PP composites were higher than pure PP matrix. However, some holes in PP matrix and some gaps between the matrix and fibers were observed due to a lack of good adhesion between CNFs and PP matrix. Since cellulose nanofibrils have a hydrophilic surface, they have a weak interaction with hydrophobic matrices, such as PP and PE; thus, an additional treatment is needed to modify CNFs surface by coating with a dispersant or by chemical modification. Wang and Sain (2007a, b) coated cellulose nanofibrils with an ethylene-acrylic oligomer emulsion (as a dispersant) and successfully produced CNFs-reinforced composites with PE and PP. The mechanical properties of the composites were slightly improved compared to pure PE or PP matrix. Freire et al. (2008) modified the surface of cellulose fibers by acylation with a fatty acid to make them compatible with PE. This surface modification apparently improved interfacial adhesion between the cellulose fibers and the matrix and therefore increased mechanical properties and water resistance of the composite.

In addition, VTT recently developed the bio-based mineral oil barrier film by coating bio-high-density polyethylene (bio-HDPE) with TEMPO-oxidized CNF. This barrier film can be used as a "bag-in-box" liner for dry foods, such as breakfast cereals. It protected the foodstuffs from mineral oil migration. More specifically, the significant reduction (>90%) in mineral oil migration after 7 days of storage was achieved as compared to non-coated bio-HDPE film and other commercial cereal bag films (“VTT files patent” 2016).

1.6.2.2 CNFs/PLA Composites

Polylactic acid (PLA) has a great potential as a biodegradable food packaging material. PLA is safe for all food packaging applications according to the US Food and Drug Administration (FDA 2002). However, PLA is brittle with very little elongation of 7.2% (Kingsland 2010) and not thermally stable (Siro and Plackett 2010). One of the solutions to these problems is the addition of cellulose nanofibrils (Iwatake et al. 2008; Suryanegara et al. 2009; Nakagaito et al. 2009; Jonoobi et al. 2010). Nakagaito et al. (2009) fabricated CNFs/PLA composites using a papermaking-like process which enabled the uniform dispersion of CNFs in PLA. They concluded that the tensile strength, Young’s modulus, and strain at break increased linearly as the CNFs contents increased. In addition, the CNFs/PLA composites exhibited constant storage modulus above glass transition temperature of PLA (T_g = 57 °C). In particular, at high CNFs content of 70 and 90 wt.%, the storage modulus did not drop up to 250 °C. This result indicated that cellulose nanofibrils network acted as a load-bearing framework, resisting the applied stress even after the PLA matrix was melt. The improvement of mechanical properties for CNFs/PLA composites was achieved even with a low CNFs content of 5 wt.% (Iwatake et al. 2008; Suryanegara et al. 2009; Jonoobi et al. 2010). Jonoobi et al. (2010) produced CNFs-reinforced PLA by twin screw extrusion, and they reported that the tensile strength and modulus increased from 58 MPa to 71 MPa and from 2.9 to 3.6 GPa, respectively, with 5 wt.% CNFs. Moreover, the addition of cellulose nanofibrils significantly improves barrier properties. Fukuzumi et al. (2009) described that 25 μm-thick PLA films had an oxygen transmission rate of about 746 ml/m^2.day.Pa, and the value substantially decreased to 1 ml/m^2.day.Pa by coating PLA film with 0.4 μm thick TEMPO-oxidized cellulose nanofibrils.

1.6.2.3 Other CNFs/Polymer Composites

Cellulose nanofibrils have been also used to reinforce other matrices, such as polyvinyl alcohol (PVA), starch, and chitosan, which have a great potential as food packaging films. First, PVA is a water-soluble and biodegradable polymer with excellent film forming property and chemical resistance. Due to these properties, it is used as a water-soluble film useful for packaging (Tripathi et al. 2009; Khan et al. 2014). Cellulose nanofibrils have been used as a reinforcement in PVA matrix, enhancing mechanical properties. Zimmermann et al. (2004) reported that CNFs/PVA composites presented up to three times higher Young’s modulus and five times higher tensile strength compared with pure PVA matrix. Such reinforcing effect of CNFs on PVA is also confirmed by others (Bhatnagar and Sain 2005; Wang and Sain 2007b; Lu et al. 2008).

Starch is the most common carbohydrate polymer used in human diets, produced from cereals and root vegetables (Singh et al. 2010). Starch has been extensively investigated as an attractive material for food packaging applications due to its environmental compatibility, wide availability, and low cost (Arora and Padua 2010).

However, it has several drawbacks, such as poor mechanical properties and high water uptake, compared with synthetic polymers. In addition, its properties can be altered easily during processing (Siro and Plackett 2010). Reinforcement with cellulose nanofibrils is one of the approaches to overcome these problems. CNFs/starch composite presents improved thermomechanical behavior (Dufresne and Vignon 1998), bending strength (Yano and Nakahara 2004), tensile strength, and tensile modulus (Dufresne et al. 2000; Chakraborty et al. 2007a) compared with pure starch. Also, the barrier properties were significantly improved when CNFs were added in amylopectin, which is one of the two components of starch. Plackett et al. (2010) reported that CNF addition reduced an oxygen permeability. 15% CNFs/85% amylopectin composite had the oxygen permeability value of 0.034–0.037 ml.mm/m^2.day.atm, and 50% CNFs/50% amylopectin composite presented the lower value of 0.02–0.013 ml.mm/m^2.day.atm at 23 °C, 50% RH.

Chitosan is a biodegradable polymer, produced from hard outer skeleton of shellfish, such as crabs and shrimps. Chitosan films may be used for food packaging applications to develop edible films or coatings, extending the shelf life of food products (Bangyekan et al. 2006; Durango et al. 2006; Campaniello et al. 2008). However, chitosan films have usually poor mechanical and barrier properties compared with synthetic polymers. Their mechanical and barrier properties can be enhanced by adding cellulose nanofibrils. Fernandes et al. (2010) reported that chitosan/CNFs nanocomposite films had up to threefold higher Young's modulus compared with pure chitosan at CNFs loading of 60%. Azeredo et al. (2010) also demonstrated that chitosan nanocomposites with 15% CNFs had comparable characteristics to some synthetic polymers, in terms of strength and stiffness. Interestingly, in another research, the addition of CNFs enhanced wet properties of the chitosan/CNFs composite by reducing the risk of creases and deformation, while the effect of CNFs on mechanical properties of dry chitosan films was small or absent (Nordqvist et al. 2007). Recently, antimicrobial chitosan/CNFs composite membranes were developed with a nitric oxide donor, S-nitroso-N-acetyl-$_{\text{D}}$-penicillamine (SNAP), and tested for food packaging applications (Sundaram et al. 2016). They reported that the membranes mixed with SNAP showed excellent water barrier property, a low water vapor permeability, and apparent effects toward inhibition of *Enterococcus faecalis*, *Staphylococcus aureus*, *and Listeria monocytogenes*.

1.6.2.4 CNFs/Ag Composites

Cellulose nanofibrils can be used as an antimicrobial film for various applications. It has been reported that cellulose containing silver nanoparticles shows very strong antimicrobial activity because silver nanoparticles and non-reduced silver ions inhibit the growth of bacteria (Son et al. 2004, 2006; Fernández et al. 2010; Li et al. 2011; Díez et al. 2011; Martins et al. 2012). Son et al. (2004) found that the ultrafine cellulose acetate (CA) fibers electrospun with very small amount of the silver nanoparticles ($AgNO_3$) exhibited antimicrobial properties. 99.9% of bacteria were reduced for CA fibers with 0.05 wt% $AgNO_3$. Fernández et al. (2010) described the antimicrobial activity toward spoilage-related microorganisms of cellulose-silver nanoparticle absorbent pads during storage of fresh-cut melon. The presence of the silver-loaded pads in melon pieces reduced the growth of mesophilic and psychotropic microorganisms.

Cellulose nanofibrils/Ag nanocomposites with antimicrobial activity have been recently developed (Díez et al. 2011; Martins et al. 2012). Díez et al. (2011) prepared CNFs/Ag nanocomposite by dipping a CNFs film into silver solution protected by poly(methacrylic) acid. They found that the growth of bacteria was inhibited around the CNFs/Ag composites. More specifically, the ratio of the surface without bacterial growth to the surface of the CNFs/Ag composite film was approximately up to 5. In contrast, bacteria grew freely around a pure CNFs film. Martins et al. (2012) also found that CNFs/Ag composites treated with polyelectrolytes showed strong antibacterial activity at low-nutrient condition.

1.6.3 Food Coating

Cellulose nanofibril coating for protecting food products has been recently invented (Zhao et al. 2014). They developed an edible composition containing CNFs in an amount of up to 1 wt% and 0.1 wt% nano-calcium carbonate (NCC) to coat and protect a plant, fruit, and vegetable. The CNFs-coated plant, fruit, and vegetable exhibited reduced leaching of functional food substrates (e.g., anthocyanins), moisture loss, and gas exchange compared with the uncoated products. CNFs coating also protected foodstuff from UV damage. The CNFs-based films had the transmittance of 7.2–27.3% for UV light, and the transmittance was further reduced by the addition of NCC. The CNFs-coated apples showed a significant increase in color intensity (chroma) after UV exposure and storage. Moreover, CNFs coating reduced weight loss of foodstuff during thawing. For instance, the weight loss after thawing of CNFs-coated apple slices was around 17%, which was lower than that of uncoated apple slices, around 21%.

1.7 Safety Issues of Cellulose Nanofibrils in Food Applications

Cellulose nanofibrils have a broad range of potential applications in food industries. However, their toxicity to humans, in particular for food consumption, still needs to be validated. Various forms of cellulose are generally recognized as safe (GRAS) food substances, according to the US Food and Drug Administration. Small cellulose particles give several benefits to food products, such as smooth consistency and stickiness, while longer cellulose fibers provide structure and a firmer texture to baked goods (Li et al. 2015). However, because cellulose nanofibrils have unusual properties not found in the bulk cellulosic materials, it might cause unknown risks to humans and the environments.

In general, it has been reported that cellulose nanofibrils have no or low toxicity (Vartiainen et al. 2011; Norppa 2012; Pereira et al. 2013; Andrade et al. 2015). Vartiainen et al. (2011) performed the in vitro study on the health and environmental safety of cellulose nanofibrils. They concluded that no inflammatory effects or cytotoxicity in mouse and human macrophages was observed after short-term (6–24 h) exposure to cellulose nanofibrils. It was also reported that CNFs did not create cytotoxic effects and damage on DNA or chromosome (Norppa 2012). Pereira et al. (2013) assessed in vitro cytotoxicity and expression of genes in fibroblast cells. Interestingly, low concentrations of CNFs (0.02–100 $\mu g.ml^{-1}$) did not have cytotoxicity, whereas high concentrations of CNFs (2000 and 5000 $\mu g.ml^{-1}$) considerably decreased cell viability and affected the expression of stress- and apoptosis-associated molecular markers. Andrade et al. (2015) performed an in vivo study with mice with diets containing different amounts of CNFs (7 wt%, 14 wt%, and 21 wt%) to investigate the effects of CNFs addition in diets. They concluded that CNFs addition did not cause harmful effects in the animal metabolism, indicating CNFs could be used as dietary supplement.

Although earlier studies reported that cellulose nanofibrils did not cause toxic effects on humans, some toxicity and safety issues still need to be validated, including long-term in vivo toxicity of CNFs and the effects of large amounts of CNFs in animal diets. Further research would be necessary to achieve a better understanding of CNFs effects to food products before commercialization of CNFs use in food industries.

1.8 Conclusions

Cellulose nanofibrils (CNFs) are one type of nanostructured cellulose with a width of below 100 nm and a length of several micrometers. CNFs are an inexhaustible and renewable biopolymer derived from lignocellulosic materials, such as wood and agricultural crops. Interestingly, the selection of raw materials affects the ease of CNFs production. Non-woody plants may be more favorable for CNFs production than wood. Non-woody cellulose fibers exist in thin primary cell walls, while wood cellulose fibers exist in thick and tightly packed secondary cell walls, and CNFs prepared from non-woody has comparable characteristics to those of CNFs from wood.

Cellulose nanofibrils have an excellent ability to form network structures due to their nanoscale dimensions, making their remarkable mechanical and barrier properties. CNFs are a gel-like material with high viscosity, but they flow once shear forces are applied. These desirable properties make CNFs a promising material in a broad range of applications, especially to food industries. CNFs can be used to develop food products, such as food additives, food packaging, and food coating. Recently, the number of studies on CNFs-based materials for food applications has been increased, increasing the likelihood of their commercialization in food industries. Further research in this field is required for a better understanding of how the structure and properties of cellulose nanofibrils affect their function, suitability, and safety for food applications including encapsulation of fat globules in food matrix.

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Nanotechnology and Shelf-Life of Animal Foods

2

Semih Ötleş and Buket Yalçın Şahyar

Abstract

Nanotechnology is an emerging technology that is coming from interest in tiny molecules. It is a matter to understand, manipulate, and control tiny molecules. Nanotechnology can be used in the food sector to enhance sensorial, nutritional characteristic of foodstuffs, and to develop health supplements and new food packaging materials. Additionally, animal foods are highly nutritious and important sources for human health. This is where nanotechnology and animal food topics relate to each other. Animal foods are required to provide and maintain safety, quality, sensing, and nutritional parameters for consumers. Thus, nanotechnology can be used to optimize and provide these requirements and needs.

Keywords

Animal food • Food nanotechnology • Shelf life • Food packaging

2.1 Introduction

Life starts with tiny molecules and/or cells that develop via different type of reactions, interactions, and chemical and/or biochemical chances. Infinite possibilities come from tiny molecules and their relations/reactions possibilities, such as vital activity, health issues for living organisms, and freshness, longevity for food products, etc. An emerging technology from interest in these tiny molecules is called nanotechnology. There are many definitions of nanotechnology. We briefly define "nano" terms as tiny molecules that range in dimension from 1 to 100 nm (nanometer). Nanotechnology is used to understand, manipulate, and control these tiny molecules (nanoparticle, nanomaterial, and nanoscale compound, such as nanotubes, fullerenes, nanofibres, nanowhiskers, nanosheets). Nanoparticles can be defined as

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tiny, discrete entities with three-dimensional shapes of 100 nm or less (Som et al. 2010). Nanomaterials can be defined as an "insoluble or biopersistent and intentionally manufactured material with one or more external dimensions, or an internal structure, on the scale from 1 to 100 nanometers" as detailed in the recent EC Cosmetics Regulation [(EC) No 1223/2009)]. Another definition is "any material that has one or more dimensions in the nanoscale range, while a nanoparticle is a discrete entity that has all three dimensions in the nanoscale" (Food and Agricultural Organization of the United Nations (FAO)/World Health Organisation (WHO), 2010) (Mildau and Huber 2010; Cushen et al. 2012; Handford et al. 2014). Nanotechnology is a multidisciplinary field from space science to food science and technology via covering broad range of materials, processing, and applications involving chemical, biological, physical, electronic, and engineering disciplines (Sorrentino et al. 2007; Sastry et al. 2010; Duncan 2011; Prasad et al. 2014, 2016, 2017). Nanotechnology-tiny particles gives chance to increased surface area and has novel and unique properties (Weiss et al. 2006; EFSA 2009; Rashidi and Khosravi-Darani 2011).

Nanotechnology application into the food sector generally aimed to enhance sensorial (taste, color, flavor, texture, consistency), nutritional (better absorption and bioavailability of nutrients) characteristic of foodstuffs and developed health supplements, new food packaging materials (better mechanical, antimicrobial, barrier properties) and also built-up nanosensors to get better monitoring and traceability conditions during storage and transportation (Chaudhry et al. 2008). Thus, nanotechnology presents safer, cheaper, long-lasting, better-designed, and smart products that have wide applications in household, communications, medicine, as well as food industry (Farhang 2007; Prasad 2014).

Animal foods can be basically defined as livestock, poultry, and aquaculture, which are highly nutritious foods, such as milk and milk products, egg, meat, and fish. Animal foods are important protein sources for human health (Kuzma 2010). This important protein source needs to maintain some parameters during the food chain, which means that nutrition, quality, safety, freshness, and sensing parameters should be met for consumer needs. Thus, shelf-life definition is coming from these types of needs, provide and maintain optimum safety, quality, sensing, and nutrition parameters during food chain as farm to fork approach to maintain high protein resources quality. After this basic definition of food shelf-life, these are not enough applications to meet consumers demand. New technologies and trends provide opportunities to inform consumers about their product knowledge and background. Consumer interest increases about what they eat and how their food grown and reaches them. Furthermore, world population increased and resources are restricted, in contrast to consumers' expectations from products—especially food—increased, which highlighted as a priority for health via the term from Paracelsus "You are what you eat." Additionally, food and food products range increased recently; even if this is a positive development, there is some confusion in consumers' minds about healthy and sufficient food selection. This food selection is one of the substantial parameters for human well being. There are numerous parameters, such as population increase, restricted resources and food waste increase, consumer knowledge, and expectation increase. These parameters forced scientists and producers to figure out novel, better, safer, healthier, easier, and cheaper solutions. Thus, nanotechnology, animal food, and shelf-life topics met.

2.2 Food Nanotechnology

Food nanotechnology, the application of nanotechnology on food and/or food packaging, such as food-related and/or contact materials, food additives and/or ingredients, nano-encapsulated food additives and supplements, nano-carriers, safer and more nutritious animal feeds—fortified with nano-supplements, antimicrobial additives, detoxifying nanomaterials—less use of farm chemicals and better control of applications (low-release pesticides), and nano-formulated agrochemicals (fertilizers, pesticides, biocides, and/or veterinary medicines) for improved efficacy and nano-biosensors for animal disease diagnostics (Shi et al. 2005; Duncan 2011; Prasad et al. 2014; Aziz et al. 2016). Nanotechnology can be a different field to use and develop to produce healthier and functional food and also enhance organoleptic properties of food. Food processing, food safety, food packaging, and agricultural production are the main topics for nanotechnology applications of food (Chaudhry and Castle 2011). The properties of materials at nano-scale can be very different from macro-materials. This can be based on nanomaterials having increased relative surface area and to the quantum effects, which can begin to dominate the behavior of matter at the nano-scale. These higher surface areas and quantum dot effects can enhance or change properties, such as reactivity, strength, and electrical characteristics (Royal Society and Royal Academy of Engineering 2004). Additionally, agricultural use of food nanotechnology can be summarized as new pesticides, targeted genetic engineering, identity preservation, agrichemical delivery, and sensors to monitor soil conditions (Duncan 2011; Prasad et al. 2014).

Benefits of food nanotechnology are more efficient food production methods and less use of agrochemicals (pesticides, antibiotics, veterinary medicines; less harm to the environment; less migration of harmful chemicals residues in food), more hygienic food processing (better food quality and safety, reducing food-borne illnesses in developing countries), novel food products with improved flavors, tastes, mouth feel (healthy/nutritious/tasteful food products), longer shelf-life of food products (contributing to reducing food waste), improved stronger, lightweight, functional packaging (reducing the cost of transportation and packaging materials in the environment), and “smart” labels to ensure food traceability, authenticity, and safety (Chaudhry and Castle 2011).

Furthermore, food packaging is an important field to keep under control for food product quality and freshness during the desired shelf-life. Packaging materials are open to development by using nanomaterials and edible and/or biodegradable materials to increase shelf-life of food and decrease waste. However, there are some limitations about using biodegradable films, and nanocomposites usage on biodegradable and edible packaging is an emerging and promising technology to cover packaging technological gaps. These nanocomposite biodegradable films are generally based on starch and derivate, polylactic acid (PLA), poly(butylene succinate, polyhydroxybutyrate, and aliphatic polyester as PCL, have better physical, good barrier, and strong mechanical properties (Kuzma and VerHage 2006; Sorrentino et al. 2007; Siegrist et al. 2008; Frewer et al. 2011).

Nanotechnology-derived food packaging materials are the largest category of current nanotechnology applications for the food sector. Food packaging applications can be emphasized via nanomaterials usage. Type of nanomaterials and packaging, such as nanocomposites (improve physical performance, durability, barrier properties, biodegradation of packaging), nano-coatings (to improve the barrier properties), surface biocides (incorporating packaging materials with antimicrobial properties acting on the packaging surface), active packaging (incorporating nanomaterials with antimicrobial or other properties, such as antioxidant with intentional release into the packaged food), and intelligent packaging (incorporating nanosensors to monitor and report on the condition of food migration possibilities into food causing a toxicological risk) have different contributions to and benefits for food packaging applications (Chaudhry et al. 2008; Bradley et al. 2011; Prasad et al. 2017).

The main problem for nanotechnology application to food sector can be defined as uncertainties about this new technology and its products, such as nanoparticles, nanomolecules, and nanoscale products physical, chemical, and/or physicochemical reactions and interactions. A study was designed to identify food applications that are more likely and less likely to be accepted by the public. There was psychometric paradigm employed and applied. The results denoted that nanotechnology food packaging was assessed as less problematic than nanotechnology foods. Additionally, analysis results showed that the importance of naturalness in food products and trust were significant factors influencing the perceived risk and perceived benefit of nanotechnology foods and nanotechnology food packaging. Even with numerous studies and research about nanotechnology and nano-scale materials chemical, physical, electrochemical, toxicological behaviors, there are still uncertainties about the health effects of these tiny molecules when consumers are exposed directly and/or indirectly via mouth, nose, and skin. There also are beneficial, promising areas for nanotechnology, such as packaging applications, decreased food waste, increased production yields, enhanced shelf-life of products, better nutritional and sensorial properties, better quality and safety controlling etc. (Siegrist et al. 2008; Schnettler et al. 2013). Additionally, some consumers are not ready and open to try new food products specially developed with new technologies, called neophobia (Pliner and Hobden 1992; Ritchey et al. 2003; Schnettler et al. 2013). In conclusion, even if there are dilemmas about application of nanotechnology into the food products, there are still promising research and studies that indicate benefits of nanotechnology. Nanotechnology application to food packaging and modification and reconstruction of self-nano-molecules particles of animal food are promising and developing research topics.

2.3 Nanotechnology and Shelf-Life of Animal Foods

When talking about nanotechnology and animal foods shelf life, animal foods are not only in the spotlight as agricultural production, they also are interested in production efficiency, animal health, feed nutritional efficiency, diseases, including zoonosis, product quality and value, byproducts and waste, and environmental footprints topics. These details and steps directly and/or indirectly affect shelf-life of animal foods. Thus, nanotechnology applications can provide effective and efficient solutions to these types of difficulties, such as improving nutrition and feeding efficiency, minimizing losses from animal diseases, animal reproduction and fertility, animal product quality, value, and safety (Kuzma 2010).

First, begin with minimization of production input while maximizing output for sustainable agriculture. Feedstock is one of the most significant inputs for animal production. Traditional feeding efficiency cannot meet the high demand of feed and cannot be up against high discharges of waste, heavy environmental burden, high production cost, and competing with other uses of the grains, biomass, and other feed materials. Furthermore, nanotechnology can enhance the nutrient efficacy and profiles of nutrient delivery of feeds to overcome feeds that are prepared and used under optimal conditions. Supplemental nutrients usage is an effective way to increase efficiency of protein synthesis and utilization of minor nutrients. Additionally, animal health can be improved by bioactive components and nutrients in addition to feed. Nanoscale delivery systems (contain liposomes, micelles, biopolymeric nanoparticles, protein-carbohydrate nanoscale complexes, nanoemulsions, solid nano lipid particles, dendrimers, and others) can add some benefit to feeding efficiency. These type of nano-scale systems have indicated numerous advantages containing better stability against environmental stresses and processing impacts, high absorption and bioavailability, better solubility, and disperseability in aqueous-based systems (food and feed), and controlled release kinetics (Chen et al. 2006). The nanoscale particles should be subject to a serious risk assessment to provide safe and responsible improvement and deployment in the products. Secondarily, some substantial animal diseases (bovine mastitis, tuberculosis, respiratory disease complex, Johne's disease, avian influenza, and porcine reproductive and respiratory syndrome) can cause significant losses in agricultural animal production. The World Health Organization (WHO) estimates that animal diseases denote as much as 17% of animal production costs in the developed world. On average, approximately 75% of animal infectious disease have been zoonotic, such as mad cow disease, Avian influenza, H_1N_1 influenza, Ebola virus, Nipah virus) (WHO 2005). Zoonotic diseases not only cause disruptive economic losses to animal producers but also enforce serious threats to human health, such as Variant Creutzfeldt -Jakob disease (vCJD). Detection and intervention can be defined as two important tools of an integrated animal disease management strategy. This strategy has an important role for reducing loss from the disease or preventing disease introduction into the animal production. Nanotechnology application to this field has the potential to allow promising changes via portable, implantable devices usage. These new developing devices gives chance to early detection of problems, additionally their easily, simply inexpensive usage possibilities (Emerich and Thanos 2006; Scott 2007). Nano-drugs and vaccines might be more effective to treat/prevent diseases than current technologies, thus reducing cost (Chen and Yada 2011).

Additionally, nanotechnology usage in animal food can be divided into groups, such as nano-meat, nano-milk, and nano-egg. Nanotechnology gives chance to produce and apply individual nanoparticles to poultry and meat industry ranging from meat design, meat safety, meat packaging, achieving food security, overcoming food allergies, enhance natural properties, eliminating pesticide use, restoring meat damage, and sensory evaluation to processes, such as separation, filtration, and encapsulation. Milk production and pasteurization also can be enhanced via nanotechnology application, such as health promotion and disease prevention, medical diagnostic, and therapeutic. Nano-egg production provide cholesterol-free eggs, yolkless, and/or reduced yolk eggs with high value protein source results (Ross et al. 2004; Kannaki and Verma 2006; Singh et al. 2011; Verma et al. 2012).

Food companies are using microcapsules to deliver food components, such as omega 3-rich fish oil. The release of fish oil into the human stomach is intended to deliver claimed health benefits of the fish oil, while masking its fishy taste (Lyons 2010; Bhattacharyya et al. 2011). These technologies are starting to improve and microcapsules are starting to change via nanocapsules. Thus, nanoencapsulation studies are started and developed concerning a variety of food-related fields. One of these fields is probiotics, which can be defined as live mixtures of bacterial species and incorporated in foods in the form of yoghurts and fermented drinks and cheese based on animal foods. Encapsulated forms of probiotics can be used to enhance shelf life of the product. Nanoencapsulation has some benefits to develop probiotic bacterial preparations, which could be delivered to certain parts of the gastrointestinal tract where they interact with specific receptors and have no or less damage during transportation to target area. These nanoencapsulated probiotics (a variety of forms are present, such as powder, capsules, and liquid) can act as nano vaccines, with the capability of altered immune responses (Vidhyalakshmi et al. 2009). Powder nanoencapsules can be stirred into food but should not be added to warmer food (warmer than room temperature), because heat will kill the bacteria. Another option for powder nanoencapsules is direct addition to diet. Yogurt, kefir (a cultured milk beverage), tempeh (made from soybeans), and kimchi (a Korean fermented cabbage dish) are the food samples for this technology.

Another possible application area for animal foods (meat, cheese, and milk products) can be edible nanocoatings, which will be used in different fields, such as meat, cheese, confectionary, bakery goods, fruits and vegetables and fast food. Nanotechnology is allowing the development of nanoscale edible coatings as thin as 5 nm. Edible nanocoatings could ensure a barrier to gas and moisture exchange and act as a vehicle to deliver colors, flavors, antioxidants, enzymes, and antibrowning agents. Thus, they could enhance the shelf life of animal foods, even after the packaging is opened (Azeredo et al. 2009; Sekhon 2010).

Food packaging is another promising area for nanotechnology application to animal food. The shelf life of packaged fresh red meat can be defined as the most frequently used and focused packaging product where microorganisms' activity plays an important role for its shelf-life. Off-odors, gas, and slime are respected as main indicators for packaged red meat shelf-life, whereas other biochemical factors, such pigment oxidation and lipid radical chain, which can cause undesirable flavors and discoloration of surface, influence shelf-life of packaged red meat. Additionally, meat microflora, myoglobin, and lipid oxidation are the parameters for the definition of fresh meat shelf-life, while microbial enzymatic and metabolite effect are secondary priority for fresh meat shelf-life definition. By the way, efficient chill-chain technology permits cutting, packaging, transportation, and retail marketing of fresh meats under suitable refrigeration condition. Modified Atmosphere Packaging (MAP) technology via different combinations of gas mixtures (such as O_2, CO_2, N_2, and CO) helps to enhance shelf-life of fresh packaged meat. These kinds of developments can be enhanced via application of nanotechnology. Alternatively, nanoscale vitamin E and/or natural antioxidants (clove, oregano, sage, rosemary, and thyme) can be used in livestock diets to delay lipid oxidation in harvested meat. Additionally, active and intelligent packaging helps to develop the safety and quality of fresh meats. Active packaging refers to packaging that has the ability to remove undesirable flavors and tastes and improve the smell or color of the packed food. Other food packaging samples are packaging materials that include metal and metal oxide nanomaterials (nano-zinc, nano-silver, nano-titanium, etc.) for antimicrobial action, gas barrier, mechanical strength, and UV protection, good antimicrobial, and stronger resistant properties (Alexandra and Dubois 2000; Chaudhry and Castle 2011; Han et al. 2011). The aim of these new technologies could be briefly classified as follows: extend shelf life, enhance safety, improve quality and packaging, enhance absorption of nutrients, warn consumers about problems, and control external and internal conditions of packaged animal food products. Even so, there are some commercialization uncertainties about nano-food packaging areas. After further investigations are performed, nanotechnology can offer a wide range of areas to improve animal food shelf-life, safety, and quality (Sun and Holley 2012; Otles and Yalcin 2015).

2.4 Conclusions

Times, life, and the universe are changing; we can never stop this changing. New generations have different types of requirements, while there are limited natural resources. Technology has developed solutions for better and sustainable living conditions. Top-down and bottom-up approaches can give a point of view to understand and identify importance and necessity of nanotechnology application in diverse fields (Yalcin and Otles 2014). Even if there are lots of dilemmas about nanotechnology application of food and variety of fields, the world needs these kinds of developments to postpone or stop scarcity, starvation, and depletion of natural sources. Thus, nanotechnology application into animal foods, especially food packaging, is becoming an essential topic, which should be developed, improved, and applied as reliable as possible. Furthermore, scientific knowledge and experiments should be increased to identify benefits of food nanotechnology.

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Nanotechnology: Meat Safety Revolution

3

Milan Z. Baltic and Marija Boskovic

Abstract

Since the need for safe, high nutritional food such as meat increases, the need to control and improve its safety also increases. Regardless of implementation of HACCP, constant monitoring, and improvements in slaughter and processing hygiene, meat safety is still an important issue from the health and economic points of view. Meat contamination may occur during all stages of production from farm to fork. Many preservation techniques are used to prevent the occurrence of food-borne diseases and control meat deterioration. Nanotechnology, involving characterization, fabrication, and manipulation of structures and inorganic or organic materials at sizes below 100 nm, is one of the innovative technologies applied in a number of science areas including food science. At the moment, nanotechnology is mainly focusing on food packaging, but nanotechnology can apply to the whole food chain presenting an excellent opportunity to detect and control pathogens, some toxins, and heavy metals; to monitor meat spoilage and extend meat shelf life; and in that sense to revolutionize the global approach to meat and, in general, food safety. Furthermore, after overcoming some obstacles in the term of regulations and safety, it can meet growing consumer demands in an acceptable and cost-effective manner.

Keywords

Food-borne pathogens • Meat spoilage • Nanosensors • Nano-packaging • Safety concerns

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3.1 Introduction

Archeological findings provide evidence that meat eating influenced human anatomy including cranial-dental and intestinal morphologic changes, erect posture, reproductive characteristics, longer life span, and brain and intellectual development. Meat is a valuable source of proteins, fats (especially some PUFA, e.g., DHA), vitamin B complex, vitamins A and D, iron, zinc, and other mineral substances, which is why meat consumption is essential for proper growth and development (Pereira and Vicente 2013; Baltic and Boskovic 2015). Meat, due to its nutritional value, gained more attention and came into focus in the human diet as the population and dietary needs rapidly increased (Saucier 2016).

Regardless of implementation of HACCP, constant monitoring, and improvements in slaughter and processing hygiene, meat safety is still an important issue from the health and economic points of view (Bošković et al. 2013). Of all the hazards from meat that can endanger consumer health, biological agents are the most important, since food-borne pathogens cause millions of illness outbreaks annually. *Salmonella* spp., *Campylobacter* spp., *Yersinia enterocolitica*, *Listeria monocytogenes*, *Escherichia coli* O157:H7, *Clostridium botulinum*, *Staphylococcus aureus*, and *Bacillus cereus* are only a few of many pathogens transmitted via meat (Burt 2004; Sofos 2008; Newell et al. 2010; Duncan 2011; Linscott 2011; Bošković et al. 2013). These bacteria can cause serious illnesses with hospitalized cases and high mortality rates, especially in children, elderly, and immune-compromised individuals. Furthermore, treatment of food-borne diseases has contributed to overuse of antibiotics, which has led to the global problem of bacterial resistance.

Apart from pathogens, spoilage microorganisms are also a matter of growing concern. Some chemical compounds that are formed during bacterial activity or as a result of biochemical processes during meat decomposition or lipid oxidation are toxic or cancerogenic (Falowo et al. 2014). Many preservation techniques are used to prevent pathogens and control meat deterioration. As technology continues to evolve, the meat industry is trying to incorporate novel technologies and apply those that can meet growing consumer demands in an acceptable and cost-effective manner.

One of the most innovative of such technologies is nanotechnology, involving characterization, fabrication, and manipulation of structures and inorganic or organic materials at sizes below 100 nm. Nanotechnology is applied in a number of fields including electronics, optoelectronic, textiles, defense, agriculture, medicine, pharmacy, and cosmetics, but it remains relatively novel in the food industry, mainly due to knowledge gaps about the immediate and long-term effects of nanoparticles on human health and legal obstacles (Azeredo 2009; Ozimek et al., 2010; Duncan 2011; Cushen et al. 2012; Coles and Frewer 2013; Baltic et al. 2013; Prasad et al. 2014). Even so, nanofoods and nano-packaging have already been commercialized in some countries. At present, nanotechnology application is mainly focused on food packaging (food contact materials), but nanoparticles and nanomaterials can be used as food additives, as flavorings, and as novel foods (Handford et al. 2014; Prasad et al. 2017). Nanotechnologies can be applied to the whole food chain, from production to processing, safety, packaging, transportation, storage, and delivery (Rossi et al. 2014). Nanotechnology presents an excellent opportunity to detect and control pathogens, some toxins, and heavy metals; to monitor meat spoilage and extend meat shelf life; and in that sense to revolutionize the global approach to meat and, in general, food safety.

3.2 Nanotechnology Application to Meat and Meat Products

In meat, as in food generally, nanoparticles and nanomaterials can be used as additives and ingredients for enhancing taste, flavor, texture, and bioavailability or incorporated in packaging materials to prevent or retard oxidation processes and microorganism growth, extend the shelf life, or monitor conditions in packaging during transportation and storage (Chaudhry and Castle 2011; Duncan 2011; Cushen et al. 2012; Azeredo et al. 2013; Rhim et al. 2013; Coles and Frewer 2013; Baltic et al. 2013; Benetti and Venturini 2015).

The use of nano-encapsulated food additives and supplements is a promising way to improve the dispersibility of fat-soluble additives in food products, enhance taste, and reduce the use of fat, salt, sugar, or preservatives (Chaudhry and Castle 2011; Baltic et al. 2013). Nano-encapsulated additives including vitamins, antioxidants, colors, flavors, and preservatives, or antioxidants and antimicrobials as nanomaterials, could find applications in processed meats (Ozimek et al. 2010). Some authors suggest that it is critical to investigate the functional efficacy of oil-in-water emulsions of nanomaterials in complex food matrices like meat products (Salminen et al. 2013; Ramachandraiah et al. 2015).

The whole concept of nanoparticle use is based on their properties in terms of improved penetrability, stability, reactivity, strength and surface area, and their optical, mechanical, catalytic, and quantum properties. Due to their size, they allow for the use of less material and new or more efficient chemical and physical reactions in comparison to larger-scale materials (Sastry et al. 2013; Cockburn et al. 2012; Ramachandraiah et al. 2015). These useful properties will cause nanotechnology to be implemented in food packaging. Nano-packaging can be classified as “improved” nano-packaging, used to improve the packaging properties (e.g., mechanical and barrier properties); “active” nano-packaging, allowing interaction with food and the environment by releasing or absorbing substances into or from the packaged food; and “intelligent” or “smart” nano-packaging, allowing monitoring of the condition of packaged food or the environment surrounding the food (Chaudhry and Castle 2011; Silvestre et al. 2011; Rhim et al. 2013; Baltic et al. 2013; Prasad et al. 2017).

Nanoparticles/nanomaterials can be applied as reactive particles incorporated into packaging in the form of nanosensors to improve quality and safety control of products (Baltic et al. 2013). Nanosensors are nanoscale devices capable of detecting and responding to physical stimuli (Joyner and Kumar 2015). Nanosensors should improve and ensure food safety by detecting pathogens and spoilage microorganisms, toxins, nutrients, chemical contaminants, gases, heavy metals, particulates, or allergens, and they respond to changes in environmental conditions of the packaged food using different mechanisms (Duncan 2011; Baltic et al. 2013; Joyner and Kumar 2015; Ramachandraiah et al. 2015). Nanosensors can be used during different stages of food production, including inspection of raw materials, online process control, and monitoring of storage conditions (Joyner and Kumar 2015). As compared to regular sensors used for these proposals, nanosensors have advantages in terms of sensitivity, specificity, and rapidity of testing (Jin et al. 2003). There are three main classes of nanosensors: (1) nanoparticle-based sensors containing different kinds of nanoparticles of complex nanoscale structures used in packaging to detect organic molecules, gases, moisture, or microorganisms; (2) electrochemical nanosensors with a detection mechanism based on binding selective antibodies (for bacteria, viruses, and protein-based toxins) to a conductive nanomaterial (nanowire, carbon nanotube, or nanocantilever) and tracking changes to the material's conductivity when the target analyte binds to the antibodies; and (3) optical nanosensors, mainly used for pathogen detection with mechanisms based on fluorescence or surface plasmon resonance (Joyner and Kumar 2015).

3.3 Nanotechnology in Meat-Borne Pathogen Control and Detection

Meat, rich in nutrients, can easily be contaminated with pathogenic bacteria responsible for numerous outbreaks of food-borne disease annually. Bacterial pathogens are considered to be the most common agents causing food-borne diseases, and among food-borne bacteria, *Salmonella* is the most common cause of illness after *Campylobacter* (Carrasco et al. 2012; Silva et al. 2013). It is estimated that non-typhoidal salmonellosis causes 155,000 deaths annually, and of 93.8 million reported cases, 80.3 million are food-borne (Majowicz et al. 2010). Major vehicles of this pathogen are eggs, poultry, and pork, as well as other types of meat and meat products (Boskovic et al. 2016). *L. monocytogenes* can be found in a variety of raw foods, including uncooked meats, but also in processed meat that can become contaminated after processing. Moreover, this bacterium commonly contaminates ready-to-eat meat products (Long et al. 2014). These food-borne pathogens, along with *E. coli*, *S. aureus*, and *Bacillus* spp., are a significant public health and economic issue, causing high morbidity and mortality in both developed and developing countries. Thus, novel and emerging methods for prevention, control, and detection of food-borne pathogens in meat and meat products are needed. A number of studies reported nanoparticles to be effective against different pathogens important from the aspect of food and particularly meat safety.

One of the most promising applications of nanotechnology in the field of preventing food-borne diseases is antimicrobial packaging. This kind of active packaging is created to slowly release nanosized antimicrobial particles, thus maintaining food safety by reducing or preventing microorganism growth (Neethirajan and Jayas 2011; Silvestre et al. 2011; Baltic et al. 2013; Wesley et al. 2014). Antimicrobial nano-packaging inhibits bacterial growth on or near the surface of the food product, which can be especially important in nonsterilized foods (Coma 2008; Ramachandraiah et al. 2015; Tornuk et al. 2015). Bacteria occur at the surface of the meat during carcass processing, while muscle interiors are generally sterile (Sofos 2005). Decontamination of the surface of packaged meat could prevent bacteria developing and spreading and, thus, contribute to product safety. Furthermore, in pasteurized foods, nano-packaging could prevent post-pasteurization recontamination (Coma 2008; Ramachandraiah et al. 2015). Nanoparticles can be incorporated in packaging in different ways: as a nanoparticle sachet in the package, by dispersing bioactive agents in the packaging, and as a coating of bioactive agents on the surface of the packaging material (Coma 2008; Ramachandraiah et al. 2015). The antimicrobial effect of nanoparticles depends on the type of nanoparticles, size, shape, surface charge, etc. (Duncan 2011). Metal and metal oxide nanoparticles are the main types of nanomaterials used for the production of active antibacterial packaging (Silvestre et al. 2011). Because of its antibacterial properties, silver nanoparticles are the most-studied and commonly used metal nanoparticles for inhibition of food-borne pathogens and are already found in several commercial applications (Silvestre et al. 2011; Azeredo et al. 2013). Ag is effective against Gram-negative and Gram-positive bacteria, fungi, protozoa, and certain viruses (Azeredo 2009; Azeredo et al. 2013; Baltic et al. 2013). Nanocomposite packaging materials containing Ag nanoparticles gradually release Ag ions and achieve their antimicrobial effects in different ways. Ag ion adhesion on the bacterial cell surface and Ag binding to the membrane cause pits to form in the bacterial cell wall, resulting in progressive release of lipopolysaccharides and membrane proteins, leading to increased permeability and cell death (Kim et al. 2007; Silvestre et al. 2011). Cellular damage by Ag atoms is also caused by penetration inside the bacterial cell which leads to inhibition of ATP production and DNA replication. Some studies showed that Ag ion also exhibited an antibacterial effect by causing oxidative stress through the catalysis of reactive oxygen species (ROS) formation (Kim et al. 2007; Duncan 2011; Azeredo et al. 2013; Rhim et al. 2013; Aziz et al. 2015). Numerous studies have confirmed the antibacterial effect of nano Ag used alone or in combination with other antibacterials on different food-borne bacteria including *E. coli* (Shahverdi et al. 2007; Damm et al. 2008; Ahmad et al. 2015), *S. aureus* (Castellano et al. 2007; Shahverdi et al. 2007; Ahmad et al. 2015), *Salmonella* Typhimurium (Saxena et al. 2010), and *L. monocytogenes* (Liu et al. 2007). Fedotova et al. (2010) reported that incorporation of Ag nanoparticles in a sausage cellulose and collagen casing exhibited strong antibacterial and antifungal effects. Ag nanoparticles have an advantage over conventional chemical antimicrobial agents and, due to the wide spectrum of antimicrobial action even at small concentrations, can be effective against microbes that are resistant to conventional chemical antimicrobials (Duncan 2011; Ramachandraiah et al. 2015). Moreover, temperature stability and low volatility are important Ag properties making it suitable for processing and practical application (Kumar and Munstedt 2005; Azeredo 2009; Silvestre et al. 2011; Azeredo et al. 2013; Baltic et al. 2013).

Apart from Ag, gold and zinc nanoparticles are also being investigated as antimicrobial nanoparticles (Silvestre et al. 2011). Metal oxide materials, such as titanium dioxide (TiO_2), zinc oxide (ZnO), silicon dioxide (SiO_2), and magnesium oxide (MgO) are the most common inorganic nanomaterials studied in the production of nano-packaging (Silvestre et al. 2011; Azeredo et al. 2013). The nanoparticles of ZnO and MgO are expected to provide more affordable and safe food packaging compared to nanosilver (Chaudhry et al. 2008; Silvestre et al. 2011). They exhibit antibacterial activity which can be attributed to the generation of ROS (Azeredo et al. 2013). It is supposed that ZnO produces ROS such as hydroxyl radicals, super oxides, and hydrogen peroxide in the presence of moisture, and these react with the bacterial cell surface and cause damage to cell contents such as protein, lipids, and DNA (Akbar and Anal 2014; Bhuyan et al. 2015). Li et al. (2009) found that ZnO nanoparticles coated onto poly(vinyl chloride)-based films inhibited growth of *E. coli* and *S. aureus*. ZnO nanoparticles also exhibited antimicrobial activity against *L. monocytogenes*, *S. enteritidis*, and *E. coli* in liquid egg white and/or culture media (Jin et al. 2009). Tayel et al. (2011) reported that ZnO nanoparticles were effective against *S. aureus* and *S. typhimurium*, which were confirmed in a later study by Akbar and Anal (2014). They found that ZnO nanoparticle films used in active packaging of ready-to-eat poultry meat sausage reduced the number of inoculated target bacteria by 7 log during 10 days of incubation at 8 °C. Panea et al. (2014) showed that ZnO with silver in a nanocomposite with low-density polyethylene can reduce the number of bacteria on chicken breast. *E. coli*, *Pseudomonas aeruginosa*, and *L. monocytogenes* on chicken breasts were inhibited by this type of packaging (Panea et al. 2014; Ramachandraiah et al. 2015). TiO_2 also exhibited an antibacterial effect against a number of pathogenic bacteria including *Salmonella choleraesuis*, *Vibrio parahaemolyticus*, and *L. monocytogenes*. Results obtained by Long et al. (2014) showed that nano-TiO_2 is very effective against *S. Typhimurium* and *L. monocytogenes*. While the TiO_2 antibacterial mechanism is similar to those reported for ZnO, the main difference is that ZnO can be activated by exposure to UV and visible light to generate ROS (Akbar and Anal 2014), but TiO_2 is activated only in the presence of UV light (Duncan 2011; Silvestre et al. 2011; Long et al. 2014). This could be a shortcoming for its use as antimicrobial agent.

Carbon nanotubes used for improving the properties of the polymer matrix also exhibited antibacterial properties against *E. coli*, possibly as a result of directly puncturing the microbial cells causing irreversible damage (Kang et al. 2007). Despite the useful properties of this nanomaterial, some studies suggest that carbon nanotubes are cytotoxic to human cells, at least when in contact with the skin (Warheit et al. 2004; Silvestre et al. 2011).

While antibacterial nano-packaging is used to control pathogens, nanosensors could ensure the safety of the product by detecting the presence of microorganisms and giving a clear visible signal of whether the food is safe or not. Similarly, to conventional biological detection methods, microbial nanosensors are based on immunological assays (antibody:antigen interactions). However, they have different optical and electrical properties, which is why their use reduces incubation and measurement times required for accurate detection and improves selectivity (Duncan 2011). Nanosensors for detecting several pathogenic bacteria including *E. coli*, *Salmonella* spp., *L. monocytogenes*, *Campylobacter jejuni*, and *V. parahaemolyticus* have been developed (Stutzenberger et al. 2010; Inbaraj and Chen 2016). Villamizar et al. (2008) suggested that nanosensors containing carbon nanotubes with attached antibodies against *Salmonella* can be used to detect these food-borne pathogens on the surfaces of foods such as chicken (Ramachandraiah et al. 2015). The use of nanosensors is a new and promising method to detect the presence of pathogens or spoilage microorganisms in the near feature (Baltic et al. 2013).

3.4 Nanotechnology in Meat Spoilage Control and Detection

Meat spoilage, which can occur during any stage of slaughtering, processing, transportation, and storage as a result of microbial spoilage, lipid oxidation, and autolytic enzymatic reactions, is an important issue for the meat industry (Dave and Ghaly 2011; Casaburi et al. 2015; Pothakos et al. 2015).

Due to its nutritional composition, high water content ($a_w > 0.99$), and pH (5.5–6.5), meat is an ideal medium for microbial growth (Buncic et al. 2014). Initially, meat becomes contaminated during slaughter and processing with bacteria in the digestive tract or from the skin of the animal. The process of meat spoilage is complex, depends on various factors, and involves many different bacterial species including *Enterobacteriaceae*, lactic acid bacteria (LAB), *Brochothrix thermosphacta*, *Pseudomonas* spp., and clostridia (Cerveny et al. 2009; Dave and Ghaly 2011; Casaburi et al. 2015; Djordjevic et al. 2016). Bacteria colonize the surface of the meat in the first phase of spoilage, while inner parts of meat are colonized later (Djordjevic et al. 2016). During mincing, bacteria from the surface are distributed throughout the meat, muscle cells lose their integrity resulting in greater surface area, and the homogenization releases nutrients which become available to bacteria. Hence, minced meat is more prone to spoilage than whole cuts (Buncic 2006), but reducing surface contamination will influence shelf life extension. Zimoch-Korzycka and Jarmoluk (2015) created biologically active edible hydrosols containing hydroxypropyl methylcellulose, chitosan, lysozyme, and nanocolloidal Ag and applied it to bovine tenderloin surface. The meat was minced and packaged under vacuum, and the effect on microbiological quality was assessed. Results showed that hydrosols containing chitosan, lysozyme, and Ag nanocolloids in different concentrations exhibited some antibacterial effect, but the addition of 1% of lysozyme and 2.0 ppm of nanocolloidal Ag resulted in the lowest total number of microorganisms during 4 weeks of storage.

In order to extend the shelf life of meat and meat products, there is a need for novel methods of eliminating or reducing spoilage microorganisms, possibly in combination with existing methods (Burt 2004; Bošković et al. 2013). Essential oils (EOs) with antimicrobial properties could be a better choice than some synthetic chemical additives, especially for organic and “natural” foods (Burt 2004; Sofos 2008; Gutierrez et al. 2009; Bošković et al. 2013). The main disadvantage of EOs is the negative impact that some components could have on organoleptic characteristics of meat. This obstacle can be overcome by adding EOs to the packaging materials rather than directly to the meat. Tornuk et al. (2015) showed that packing Turkish-type fermented sausage in linear low-density polyethylene packaging with incorporated nano-clays grafted with EO compounds thymol, eugenol, or carvacrol suppressed the growth of total mesophilic aerobic bacteria, LAB, yeasts and molds, and *Enterobacteriaceae* compared to the control. The antibacterial effect of the packaging method depended on the EO component used, and nano-packaging with thymol or carvacrol had a greater effect than active nanocomposite films with grafted eugenol. Low-density polyethylene nanocomposite films were also used in the study conducted by Azlin-Hasim et al. (2015) where Ag nanoparticles were incorporated into packaging material in different concentrations, and their effect on total viable bacteria, psychrotrophic bacteria, *Pseudomonas* spp., *B. thermosphacta*, LAB, total coliforms, and *E. coli* in chicken breast fillets was assessed. In the chicken meat wrapped with Ag/LDPE nanocomposite films, bacterial counts were lower than in controls during the whole storage period, but differences in the bacterial count were more pronounced during the first days of storage.

Metal oxide nanoparticles can inhibit growth of spoilage bacteria. It was reported that TiO_2 nanoparticles showed an antibacterial effect against *Pseudomonas fluorescens* and *Macrococcus caseolyticus*, bacteria often reported to cause spoilage of chicken and other types of meat (Wang et al. 2014). ZnO/LDPE nanocomposite films also exhibited an antibacterial effect on bacteria on chicken breast fillets (Panea et al. 2014). Results from these studies indicated that LDPE nanocomposite films containing different nanoparticles with antibacterial properties could potentially be used to extend meat shelf life and increase meat safety.

It is not only meat that contains microorganisms but meat juices as well. Absorbent pads are widely used in modern packaging strategies to keep meat or meat product fresh, protect packaging systems from unsanitary meat juices, and create an aesthetically attractive package. When absorbing meat juices, these pads become contaminated and, thus, serve as a reservoir for bacteria and support their growth. Cellulose absorbent pads previously soaked in 1% of Ag nanoparticle solution effectively reduced spoilage microorganisms (total aerobic bacteria, LAB, *Pseudomonas* spp., and *Enterobacteriaceae*) in modified atmosphere-packaged (MAP) beef (Fernández et al. 2010). Impregnation of absorber pads with different nanoparticles could affect meat microbiological quality and reduce the risk of foodborne bacterial growth or delay spoilage.

During storage spoilage microorganisms use nutrients from meat such as glucose, lactic acid, nitrogenous compounds, and free amino acids (Skandamis and Nychas 2002; Nychas et al. 2008). Different catabolic by-products are formed as a result of their metabolism and due to decomposition of meat compounds. The volatile fraction of the microbial catabolites which are spoilage/freshness indicators that affect sensory characteristics of the meat includes organic acids, volatile fatty acids, ethyl esters, sulfur compounds, ketones, aldehydes, alcohols, ammonia, and other molecules (Casaburi et al. 2015). Some of these compounds, e.g., biogenic amines, are toxic and pose a health risk (Jairath et al. 2015). Different kinds of nanosensors have been developed in order to detect gaseous amines, indicators of fish and meat spoilage, at the ppt level using fluorescence quenching of nanofibrils of perylene-based fluorophores or at the ppm level using conductance changes in composites of tin dioxide (SnO_2) nanoparticles and TiO_2 microrods (Hernández-Jover et al. 1996; Zhang et al. 2008; Zhang and Zhang 2008; Duncan 2011). Liu et al. (2015) developed chemiresistive detectors for amine vapors made from single-walled carbon nanotubes by non-covalent modification with cobalt meso-arylporphyrin complexes which increases sensitivity toward amines. This detector was used to detect total volatile basic nitrogen (TVBN) emission in pork, chicken, salmon, and cod during 4 days storage at two different temperatures. Changes were not detected in food stored at 4 °C, which was expected considering that low temperatures inhibit the growth of number bacteria during the short period of storage. When food was stored at 22 °C, an increase in response was seen after the first day. Even it is not practiced to store meat above the temperature of refrigeration, many studies proved that storage temperature of meat and meat products in households is higher than those recommended. TVBN content is an important index of meat freshness and increases in meat and meat products during storage as a result of spoilage by either bacterial or enzymic degradation (Cai et al. 2011). Results from these studies emphasize the potential of this nanosensor in meat spoilage detection.

Oxygen nanosensors could play an important role, as this gas (or its absence) is crucial to bacterial metabolism. Changes in oxygen content in MAP as well as in vacuum packaging could indicate bacterial activity and evolution of spoilage (Valdés et al. 2009). Oxidation is, apart from a result of bacterial growth, a limiting factor for meat shelf life. Lipid oxidation led to meat quality deterioration and accumulation of toxic compounds, which could be a threat to the health of consumers (Falowo et al. 2014). The use of nanosensors allows easy monitoring of the oxygen content of a package headspace without package destruction, providing at the same time visual detection of changes for consumers (Baltic et al. 2013). Photo-activated indicator ink for package oxygen detection has been developed, based on nanosized TiO_2 or SnO_2 particles and a methylene blue reaction. In response to low quantities of oxygen, the indicator gradually changes color, and the level of change depends on the amount of O_2 exposure – it is bleached when there is no exposure and blue when fully exposed (Azeredo 2009; Mills and Hazafy 2009; Duncan 2011). Li et al. (2004) reported that nanocrystalline TiO_2 deposited on glass and acetate films effectively created deoxygenated closed environments. Thus, nanocomponents can be used as oxygen scavengers within the packaging to eliminate or reduce a level of oxygen on an acceptable or desirable level. Similarly, SiO_2 gallic acid nanoparticles were capable of scavenging free radical diphenylpicrylhydrazyl (DPPH), which implies they could be used as novel nanoantioxidants (Deligiannakis et al. 2012; He and Hwang 2016). In order to prevent oxidation, nanoparticles can be used as antioxidant carriers. For example, polymeric nanoparticles are suggested as being suitable for the encapsulation of bioactive compounds (e.g., flavonoids and vitamins) (Pool et al. 2012; He and Hwang 2016). Moreover, packaging film enriched with silicate or other nanoparticles improved film permeability and reduced the ingress of oxygen and other gases; this prevented or delayed spoilage (Neethirajan and Jayas 2011).

Oxygen nanosensors provide information about the integrity of packaging, and this noninvasive technique in combination with oxygen scavenger and improved packaging can be used to prevent and control oxidation processes in meat.

3.5 Nanotechnology in the Control and Detection of Other Hazards Related to Meat

Apart from biological hazards, chemical and physical hazards also pose a serious threat to human health. Although meat thermal processing, especially at high temperature, reduces the risk of meat-borne diseases, this practice may cause the formation of some carcinogenic or mutagenic compounds (Navarro et al. 2004; Jägerstad and Skog 2005; El-Badry 2010; Aaslyng et al. 2013; Boskovic and Baltic 2017). Heterocyclic aromatic amines (HAAs) and polycyclic aromatic hydrocarbons (PAHs) are most common (Ferguson 2010; Berjia et al. 2014). These genotoxic substances act directly on DNA, causing point mutations, deletions, and insertions, and initiate carcinogenesis for a number of cancers (Sutandyo 2010; Ruiz and Hernández 2014). Their formation depends on meat type, temperature, and method of cooking (barbecuing/grilling, frying) (Jägerstad and Skog 2005; El-Badry 2010; Aaslyng et al. 2013; Berjia et al. 2014). Since these substances pose a risk to human health, their control is an important step. At the moment, chromatographic methods including GC or HPLC are the main methods to determine PAHs in foods, but low concentrations, especially in complex foods containing various interfering compounds, cannot always be detected (Moazzen et al. 2013). Moazzen et al. (2013) reported that magnetic solid-phase extraction based on magnetic carbon nanotubes, which possess excellent adsorption capabilities, as an extraction medium for PAHs from grilled lamb, beef, and chicken meat, simplified the procedure by eliminating the column passing and filtration steps. This shows that the use of nanotechnology in PAH detection could improve the sensitivity and reliability of the detection methods. It is replaced with this sentence : Although meat thermal processing, especially at high temperature, reduces the risk of meat-borne diseases, this practice may cause the formation of some carcinogenic or mutagenic compounds (Navarro et al. 2004; Jägerstad and Skog 2005; El-Badry 2010; Aaslyng et al. 2013; Boskovic and Baltic 2017).

The use of growth-promoting hormones in food-producing animals is forbidden in the EU and some other countries. However, hormone residues in animals are still a matter of concern. The US Food and Drug Administration allows the use of some endogenous hormones (e.g., testosterone propionate, estradiol, estradiol benzoate, progesterone, and bovine somatotropin) in cattle and zeranol in sheep to increase weight gain, improve feed efficiency, or increase milk production (Nachman and Smith 2015). Hormones are not approved for use in poultry or swine, but there is still illegal usage of these substances in their breeding (Nguyen et al. 2012). Humans can be exposed to these hormones and/or their biologically active metabolites by consuming edible tissues, e.g., meat or liver, where these substances accumulate (Andersson and Skakkebaek 1999; Afeiche et al. 2014). Many of these residuals could affect human health, which highlights the need for rapid and sensitive detection of hormones in animal products. Nguyen et al. (2012) reported that a fluorescence resonance energy transfer-based nanosensor, consisting of CdTe quantum dots coated with the clenbuterol-recognizable agent naphthol and diazotized clenbuterol, can be used for the detection of clenbuterol. This thermostable hormone, which is responsible for cancers, poisoning, heart failure, and hypertension, was detected at levels up to 10 pg ml^{-1} (Nguyen et al. 2012).

Furthermore, mycotoxins are yet another important issue from the aspect of food safety. Mycotoxins are low molecular weight toxic secondary metabolites produced by fungi, and they occur naturally in a range of plant products (Ramesh et al. 2013; Abd-Elghany and Sallam 2015). They can be found in different foods, mainly cereals, peanuts, and tree nuts, but mycotoxin residues can occur in milk, eggs, and meat as a result of metabolism and deposition after animals ingest contaminated feed (Brown et al. 2001; Ramesh et al. 2013). Mycotoxins can also occur as a result of the direct growth of toxigenic molds on the outer layers of meat products (Bailly and Guerre 2009) or from the addition of spices (Fazekas et al. 2005; Abd-Elghany and Sallam 2015). The aflatoxins deoxynivalenol, zearalenone, ochratoxin, fumonisin, and patulin are major toxins found in food and feed (Rai et al. 2015). Mycotoxins have hepatotoxic, nephrotoxic, teratogenic, carcinogenic, or immunosuppressive effects (Felizardo and Câmara 2013; Ramesh et al. 2013; Abd-Elghany and Sallam 2015). Since the elimination of mycotoxins from the human diet, as in the case of bacteria, is impossible, there is a need for constant monitoring and rapid and sensitive analytical methods which can detect low amounts of mycotoxins. In literature, there are a few reports of detection of mycotoxins in feed or food using nanosensors containing carbon nanotubes, nanowires, nanoparticles, quantum dots, nanorods, and nanofibers (Rai et al. 2015). Cha et al. (2010) demonstrated that the use of monoclonal antibodies coupled with magnetic nanoparticles coated with SiO_2 showed greater efficiency in detection of zearalenone and aflatoxin B_1 than a commercial immunoaffinity chromatography method. Yao et al. (2004) constructed an electrochemical biosensor for sterigmatocystin using multiwalled carbon nanotubes modified with an enzyme, aflatoxin-detoxifizyme. This sensor was effective, but further investigation on the effects of temperature, pH, and other factors on detection of mycotoxin and applicability of the method should be conducted.

One of the global concerns associated with nutrition is food allergies, which affect up to 220–250 million people, mainly children (Pawankar et al. 2011; Lim and Ahmed 2016). While an allergy to fish protein is common (Mills 2011), allergy caused by consumption of mammalian proteins has rarely been reported in the literature (Palacios Benito et al. 2002; Theler et al. 2009). This is probably because meat is most often consumed cooked and the major meat allergens are thermolabile (Theler et al. 2009). Even so, pork and beef allergies have been described, and serum albumin has been recognized as an important allergen linked to meat allergy (Kim et al. 2011; Lim and Ahmed 2016). Lim and Ahmed (2016) showed that porcine serum albumin can be detected at levels of 0.5 pg/mL with an immunosensor constructed by first electrochemically reducing 4-carboxyphenyl diazonium salt, which had been electrochemically generated in situ, to a stable 4-carboxyphenyl layer on carbon nanofiber-modified screen-printed electrode. Pork is often added to meat products because of its low cost, and the described sensor can be used to detect the presence of this meat (Lim and Ahmed 2016).

Heavy metals such as cadmium, lead, arsenic, and mercury are more commonly contaminants of fish but are more rarely meat contaminants. They have a negative impact on human health and can be harmful to different organs at very low levels (Engel et al. 2015). Darbha et al. (2007) detected mercury in fish (2 ppt), by using gold nanoparticle-based fluorescence resonance energy transfer. Highly fluorescent rhodamine B molecules were self-adsorbed onto the surface of gold nanoparticles, and their release in the presence of mercury was followed with a very distinct fluorescence signal change. The same sensor was also used to detect this heavy metal in soil and water, and results showed that the sensitivity of this method to detect mercury was about 2–3 orders of magnitude higher than the US Environmental Protection Agency standard limit. Hung et al. (2010) developed a simple, rapid, and cost-effective method based on using label-free gold nanoparticles and alkanethiols for colorimetric detection of mercury, silver, and lead ions in water. A highly sensitive nanosensor for heavy metal ion detection in liquid was also developed by Wu et al. (2010). This nanosensor was constructed by conjugating quencher-labeled DNAzymes onto the surface of carboxyl-salinized quantum dots and was able to detect copper and lead in low concentrations (0.2 and 0.5 nM, respectively) in a short period of 25 min. This sensor was also tested for multiplex detection resulting in negligible cross talk between the examined metals.

Furthermore, nanosensors can be used to detect other contaminants including small molecules like melamine, associated with renal toxicity due to crystal formation and carcinogenicity (Buur et al. 2008). Despite the fact that melamine is mainly a contaminant of infant formulas and pet food, techniques based on nanotechnology have been developed to detect this chemical in meat and fish (Liu et al. 2010). Nanosensors based on gold nanoparticles (AuNPs) functionalized with cyanuric acid groups selectively bind to melamine. This led to aggregation which caused AuNPs to undergo a reproducible, analyte-concentration-dependent color change from red to blue, making the presence of low amounts of melamine (2.5 ppb) visible (Ai et al. 2009; Joyner and Kumar 2015).

3.6 Nanotechnology Safety Concerns

Lack of data about the effects of nanoparticles on human health and the environment, public acceptance and regulations are major limiting factors for nanotechnology practical application in the food sector.

Nanoparticles can enter the body via dermal contact, inhalation, and ingestion and even parenterally in the case of nanotechnology-based medical devices (Silvestre et al. 2011; Cushen et al. 2012; Rhim et al. 2013; Baltic et al. 2013; Dimitrijevic et al. 2015). Workers often have the highest exposure and are first to be exposed to nanoparticle contact (Schulte et al. 2014). In terms of food and particularly meat production, inhalation and dermal contact are routes of transmissions almost exclusively related to workers in nanomaterial-producing factories (Silvestre et al. 2011). Among food industry workers and consumers, ingestion is the most important means of nanoparticle entrance (Cushen et al. 2012). As explained, nanoparticles have different properties from the same large-scale materials; so in the context of food safety, nanoparticles are more reactive, more mobile, and likely to be more toxic. Hence, even if additives used in meat and meat products are classified as GRAS, they still need to be reexamined when used at the nanoscale level (Wesley et al. 2014). According to Chaudhry and Castle (2011), food products containing natural food nanostructures are areas of least concern from the food safety aspect because these natural components are digested or solubilized in the gastrointestinal tract and are not bio-persistent. In contrast, food products containing encapsulated food additives in nanosized carriers, even if not bio-persistent, could carry the encapsulated substances across the gastrointestinal tract. Food products containing insoluble, indigestible, and bio-persistent nano-additives such as metals or metal oxides are an area of major concern (Chaudhry and Castle 2011). The toxicological effects of nanoparticles depend mainly on chemical composition, diameter, properties, method of entrance to the body, and target tissue (Baltic et al. 2013). After entering through the digestive tract into the circulatory system, the liver and the spleen are the two major organs for distribution (Silvestre et al. 2011). The small size and large surface area of nanoparticles allow their easy dispersion and invasion of anatomical barriers in the human body (Jain et al. 2016). Some nanoparticles are able to cross the blood-brain barrier, enter cells and organs, and interact with metabolism in different ways (Leroueil et al. 2007; Coles and Frewer 2013) or migrate into the fetus (Silvestre et al. 2011). Genotoxicity and carcinogenicity are the reported adverse effects of nanoparticles which draw the most attention (Dimitrijevic et al. 2015).

The benefits of nanotechnology are well documented, but knowledge gaps on the bioavailability, bio-distribution, and the effect of nanoparticles in the human body are areas that principally influence public acceptance. Public attitudes toward nanotechnology and novel technology in general are influenced by numerous factors including perceived benefits and risk; social, economic, and political environments; religious beliefs and moral concerns; as well as trust in the industry producing nanotechnology foods (Brossard and Lewenstein 2009; Scheufele et al. 2009; Macoubrie 2006; Siegrist et al. 2007; Stampfli et al. 2010; Silvestre et al. 2011; Baltic et al. 2013; Frewer et al. 2014). It is expected that the media will affect the public perception of nanotechnology in either a positive or negative direction (Frewer et al. 2014).

In general, people are skeptical when it comes to innovation and use of new technologies in the field of food production, and nanotechnology is not an exception (Baltic et al. 2013). Consumers have preferred so-called natural foods and perceived naturalness, or lack of it could be a factor that influences the perception of nanotechnology use in food production (Siegrist et al. 2007; Coles and Frewer 2013; Baltic et al. 2013). The success of nanotechnology implementation in the food sector and commercialization depends mainly on the willingness of consumers to buy and consume such products (Giles et al. 2015; Roosen et al. 2015). A major issue is the fact that consumers are not familiar with the term “nanotechnology” or with the potential benefit of this technology when applied in the food chain (Frewer et al. 2014). Siegrist et al. (2007) suggests that nanotechnology packaging is perceived as being more beneficial and presents less health risk than nanotechnology foods. Furthermore, consumers have assessed that application of nanoparticles directly in food is the most critical method for nanotechnology application mainly because of the low control levels (Siegrist et al. 2007). Results of studies examining consumer acceptance showed consumer perceptions toward food nanotechnology vary in different countries. Most of the studies confirmed that public knowledge about nanotechnology is very limited. Consumers in the United States expected many advantages from nanotechnology, including production of safer and better food, and despite potential risks, were willing to use specific products containing nanoparticles if benefits were high.

In contrast, Europeans and Australasians appeared to be less open to agri-food nanotechnology than other population groups and more open to the use of nanotechnology in some other fields not associated with food production (Cobb and Macoubrie 2004; Currall et al. 2006; Castellini et al. 2007; Siegrist 2008; Kahan et al. 2009; Silvestre et al. 2011; Giles et al. 2015). Also, when expert and consumer attitudes were compared, experts, more so than consumers, found nanotechnology more acceptable if it were to be used directly in foods (Giles et al. 2015). One possible explanation might be due to the fact that experts have greater knowledge and possess more information about risks and benefits of nanotechnology use. Hence, for nanotechnology implementation in everyday life, it is crucial to inform and educate consumers, because, ultimately, humans, animals, and the environment will be exposed to nanoparticles during the production, usage, and disposal of nanoproducts in any field not just during food production. To introduce nanofood, transparent public discussion must involve scientists from fields including food safety, public health, and medical and environmental experts.

3.7 Conclusions

The use of nanotechnology offers great opportunities in many different fields including the agri-food sector, where it is still in the early developmental stage. This technology can be applied in various ways in food in the form of nano-additives or incorporated in nano-packaging to prevent, reduce, or detect the presence of different hazards in order to ensure safety and quality of products. Considering meat as one of the most nutritious and widely consumed foods, there is a need for further research into nanoparticle and nanomaterial applications in/on this matrix. Despite the diverse benefits and the fact that some nanofood is already available on the market, various issues remain concerning nanotechnology application in food. This is reflected mainly in the lack of information about effects on human health and the environment, public acceptance, and regulations. Whether scientists and industry will try to find a way to overcome these obstacles and whether nanotechnology will find a future role in meat safety and in general food safety remain to be seen.

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Marine Nanofactories in Food Industry: Friend or Foe

4

Loganathan Karthik, Arivarasan Vishnu Kirthi,
and Zhiyong Li

Abstract

This book chapter introduces how marine Actinobacteria-inspired nanoparticles are used in the food industry. Food nanotechnology is a zone of rising intrigue, which leads to an entire universe of fresh substantial results for the nourishment and food business. These modules of the nanotechnology application and their functionalities at present led to the building of the sustenance, which includes alterations of the plastic material limitations, combining the dynamic segments that led to the practical qualities past those of routine dynamic bundling, and the detecting and motioning of important data. Nano food bundling or packaging materials may expand nourishment life, enhance sustenance well-being, inform buyers that nourishment is polluted or ruined, and repair the tears and secrete the additives to increase shelf life of the food materials. The role of nanotechnology and its abiding functionalities can be used to identify the specific microscopic organism in the bundling process or lead to more grounded flavours and to increase shade time and the well-being of the hindrances and their ill effects on food. The role of nanotechnology is to hold extraordinary guarantee to give advantages inside of sustenance items as well as around nourishment items. Indeed, nanotechnology presents new risks for the advancement in the nourishment business at a monstrous rate, yet vulnerability and well-being concerns are likewise rising. EU/WE/worldwide enactments that regulate the usage of nanotechnology functionalities in the sustenance are very small. Also, the enactment law of the present time is unsatisfactory for the instructions and specifications

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provided for nanotechnology. Bio-inspired nanoparticles is a recently emerging field in the nano world. Hence, marine Actinobacteria-based nanoparticle synthesis may play a major role in food industry.

Keywords
Marine Actinobacteria • Food industry • Nanoparticles

4.1 Introduction

The term "nanotechnology" is derived from the Greek language and means "dwarf or little." The unit of nanometer can be denoted as the thousandth part of the thousandth part of the metre, i.e., 10^{-9} m. A single nanometer is an equivalent to 60,000 times smaller than the human hair compared with the size of the smallest virus. Furthermore, the diameter of the DNA is approximately 2.5 nm. Therefore, the role of nanotechnology forms a large portion of the breadth of DNA to 1/20 of the platelet diameter (Dingman 2008; Keshwani et al. 2015). Two approaches are common in nanoparticles fabrication: "top-down" and "bottom-up." The "bottom-up" approach is a more flexible and inexpensive preparation (Heath 1999; Xia et al. 2013). Bio-inspired nanoparticles a recently emerging field in the nano world. In recent years, there has been much study of bio-inspired nanoparticles fabrication, although marine Actinobacteria-based nanoparticles fabrication was still unexplored completely. In marine ecosystem, marine microorganisms are known to interact with metal ions and able tolerate high metal salt concentration.

The biological method for production of nanoparticles is great improvising and a good alternative due to the involvement of the nontoxic capping agents, lesser hazardous agents utilization, and the selection of environmentally friendly solvents (Duan et al. 2015). Most bio-inspired nanoparticle are synthesized by opportunistic pathogens, such as *Bacillus*, *Pseudomonas*, etc. In environmental concern, plants also can be used. Hence, marine Actinobacteria inspired nanoparticles fabrication is very good alternative for food industry. Marine Actinobacteria are well-known producer of antibiotics and is known for nanoparticles fabrication. Marine Actinobacteria-inspired nanoparticles showed wide range of biological activities, such as antibacterial, antifungal, anticancer, anti-biofouling, anti-malarial, antiparasitic, antioxidant, etc. (Baker et al. 2013).

The chemical reduction of nanoparticles from the use of chemically hazardous substances has disastrous consequences on the environment and living kind. Preparations of the silver and silver-based nanoparticles as the stable, collodial dispersions in the water or the organic solvent. The most frequently used chemicals for the reduction process include borohysride, citrate, ascorbic acid, and elemental hydrogen. It also is important to use the protective agents to preserve and stabilize the dispersive nature of the nanoparticles, especially metal-based nanoparticles, which proved useful. For the protection of the nanoparticles, the most commonly used method is the coating of the agents or the capping agents to absorb onto the surface of the nanoparticles and leading to avoidance of agglomeration process (Oliveira et al. 2005; Bai et al. 2007).

Recently, the attraction to the biosynthetic methods that use reducing agents, such as the polysaccharides from the plant extracts, bacteria, and fungal species; the green chemistry has therefore arisen as a simple and clever alternative to chemical synthetic process for preparation of metal nanoparticles, such as the AgNPs (Prasad 2014; Prasad et al. 2016).

Interest for health-improving foods has expanded considerably over the past years because of development of the planet populace and an expanded impression of horrible ways of life. By 2050, the number of people older than aged 65 years is expected to achieve an aggregate of approximately 1.5 billion, which is equal to 16% of the world's populace; in 1950, it was just 5% (Haub 2011). As the populace ages, there is will be expanding interest for a conceivably constructive outcome on well-being past fundamental sustenance—utilitarian nourishments.

Furthermore, it is fascinating to note that nanomaterials are so small, even microorganisms would require a magnifying lens to see them (Yaktine and Pray 2009). The ideology of nanoparticles are very much accepted by the scientific and medical world, because these particles are sized in the range of 100 nm, which makes them fit for novel applications and has concrete advantages. The nanomaterials are subjected to various physical and chemical characterization processes; these nanoparticles are unique in relation to their bulk counterparts compared with bigger particles (Chaudhry et al. 2008; Chau 2015). Newer age of advancement for the potential in nourishment (or) food nanotechnology has been included in the food bundling/or packaging, the food substances and supplements because of their capacities and utilizations of the nanoparticles (Chaudhry et al. 2008). A huge mass of dollars is paid in the global race for use of nanotechnology in food production, processing, and packaging. The cholesterol-lowering food materials and/or the food additives are having wider scope in the business sector, for example, the Benecol margarine spreads and cream cheese containing esterified fat-soluble phytosterols or stanols from plant extracts (Chen et al. 2008, 2011).

4.1.1 Marine Actinobacteria

Currently, 60% of natural products drugs are available in the market (Newman and Cragg 2007). In this marine environment, associated microorganisms become a big pool of new natural products. Particularly, marine Actinobacteria play a significant role in finding new structurally diverse compounds (Fenical and Jensen 2006). The isolated and the characterized secondary metabolites from the marine Actinobacteria have depicted certain antibacterial, anticancer, antiviral, anti-angiogenesis, anti-inflammatory, antimalarial, and some antitumour activities. There have been investigations and the functional gene screening of the Actinobacteria strains for natural compounds and associated products, for example, polyketides, isoprenoids, phenazines, indolocarbarbazoles, and sterols. These products were synthesized by non-ribosomal peptide synthetases and polyketide synthases.

4.2 Marine Actinobacteria Nano Factories

Compared with terrestrial microorganisms, marine microorganisms are known to interact with metal ions in marine ecosystems. Hence, it can reduce metallic ions quickly for the formation of nanoparticles of required shape and controlled size (Baker et al. 2013). Marine microorganisms have unique mechanisms to survive in high salt concentration and can tolerate toxicity of different metal ions. Due to chemical reactions between marine water and mineral salts, the metal-rich effluent is formed (Colmer and Hinkel 1947). Those microorganisms that can grow in this environment could be good choice for the synthesis of nanoparticles. Only a few reports are available among publishers that show the nanoparticles fabricated by the member of actinomycetes possess potential biocidal activities against various pathogens (Golinska et al. 2014). Most of the paper reported that engineered nanoparticles are more toxic. On the other hand, bio-inspired nanoparticles are less toxic, because attached biomolecules from microorganisms can nullify the toxicity (Karthik et al. 2013a).

4.2.1 Nanoparticles-Green Synthesis

The capping agents plays major role in stabilization of the synthesized nanoparticles to control the size, morphology, and avoid aggregation. Several capping agents currently used, such as Heteroatom-functionalized long-chain hydrocarbons, polymers, dendrimers, and block co-polymers. In green synthesis, these three act as a capping agent, such as polysaccharides, biomolecules, and small molecule. In these, particularly using small molecules, the nanoparticles have specific shapes or dimensionalities. It is generally organic compound in nature (You et al. 2013). Hence, it has environmental and economic importance. Marine Actinobacteria could be used for synthesis/or production of different natural products, such as polyketides, isoprenoids, phenazines, peptides, indolocarbarbazoles, sterols, and others (Fenical and Jensen 2006). These organic compounds play a major role in nanoparticles fabrication, are nontoxic, and can be used in the food industry (Fig. 4.1).

Reducing agents are the next important thing in nanoparticle synthesis. Mostly, sodium borohydride ($NaBH_4$), hydrazine (N_2H_4), and formaldehyde were used as a reducing agent. After reaction, these chemicals make a circuit around the final product. The role of reducing agents is well played by the proteins and peptides alike. The comparison among the prokaryotic bacterial species and the eukaryotic fungal and the Actinobacteria are studied and well characterized by the presence of increased concentrations of proteins. The amino acids and the role in the reduction and synthesis of Au nanoparticles have been well-characterized (Tan et al. 2010). They found that all 20 natural R-amino acids are capable to bind with Au. The presence of weak binding affinity and the related reducing ability results in chelation and the reduction of the metal ions. Recently, Karthik et al. (2014) isolated a novel peptide from marine Actinobacteria. Mostly nitrate reductase from marine Actinobacteria act as a reducing agent (Karthik et al. 2013b). The whole cell or

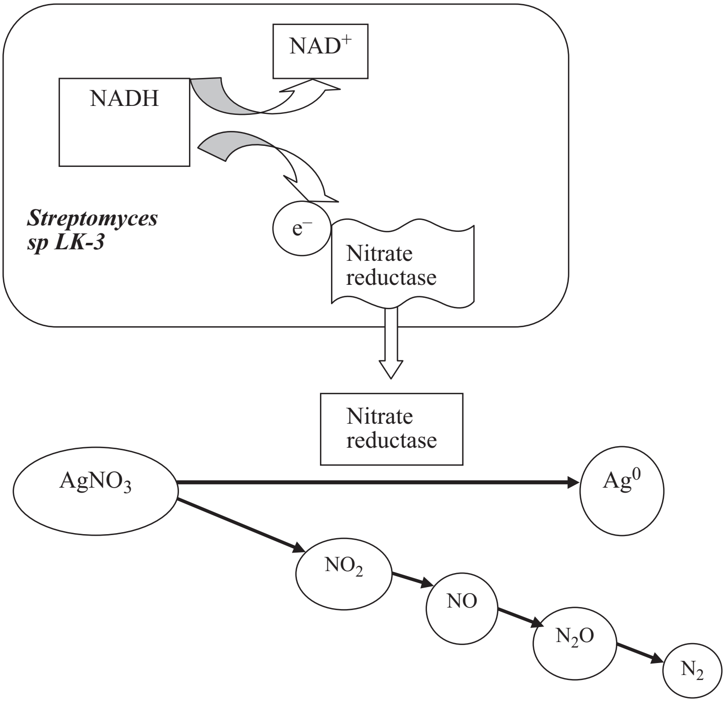

Fig. 4.1 Proposed mechanism for the synthesis of silver nanoparticles (Karthik et al. 2013b)

culture supernatant from the microbial resources and the aqueous or solvent-based extract from plants have been utilized in the nanoparticles generation (Kirthi et al. 2011; Marimuthu et al. 2013; Venkatesan et al. 2014; Rajakumar et al. 2015). Therefore, the marine Actinobacteria could be a very good alternative for the hazardous reducing agents.

Different metal nanoparticles are fabricated by Actinobacteria, such as silver, gold, zinc, and copper, with antimicrobial activity against a broad spectrum of pathogens and multidrug-resistant pathogens (Table 4.1). Based on its wide range activity, they are termed as the new generation of antimicrobials (Rai et al. 2012; Aziz et al. 2016).

Table 4.1 Actinobacteria-inspired nanoparticles and its activity against broad spectrum of organisms

Actinomycetes used for synthesis	Type of NPs	Intracellular/ extracellular	Size (nm)/ shape	Target organisms
Nocardiopsis alba MSA10	Silver	Extracellular	20–50/ spherical	*Bacillus subtilis* (MTCC 1305), *Bacillus cereus* (MTCC 1307), *Staphylococcus aureus* (MTCC 2940), *Escherichia coli* (MTCC 739), *Vibrio cholera* (MTCC 3906), *Vibrio para- haemolyticus* (MTCC 451), *Vibrio vulnificus* (MTCC 1145), *Pseudomonas fragi* (MTCC 2458), *Salmonella typhi* (MTCC 734)
Streptomyces sp. JAR1	Silver	Extracellular	60–70	*Enterococcus faecalis*, *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhimurium*, *Shigella* sp., *Proteus mirabilis*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Candida tropicalis*, *Fusarium* sp., *Scedosporium* sp. JAS1, *Ganoderma* sp. JAS4, *Aspergillus terreus* JAS1
Streptomyces sp. LK3	Silver	Extracellular	5/Spherical	*Rhipicephalus microplus,* *Haemaphysalis bispinosa*
Nocardiopsis sp. MBRC-1	Silver	Extracellular	45/ Spherical	*Escherichia coli*, *Bacillus subtilis*,
	Silver	Extracellular	5–50	*Staphylococcus* sp., *Pseudomonas* sp., *Bacillus* sp.
Streptomyces albidoflavus CNP10	Silver	Extracellular	10–40/ Spherical	*Bacillus subtilis*, *Micrococcus luteus*, *Escherichia coli*, *Klebsiella pneumonia*
Streptomyces hygroscopicus BDUS49	Silver	Extracellular	20–30/ spherical	*Bacillus subtilis* KCTC3014, *Enterococcus faecalis* KACC13807*,* *Escherichia coli* KCTC1682*,* *Salmonella typhimurium* KCCM40253*,* *Candida albicans* KACC30069*,* *Saccharomyces cerevisiae* KCTC7906

(continued)

Table 4.1 (continued)

Actinomycetes used for synthesis	Type of NPs	Intracellular/ extracellular	Size (nm)/ shape	Target organisms
Streptomyces sp. VITPK1	Silver	Extracellular	20–45	*Candida albicans* MTCC227, *Candida tropicalis* MTCC184, *Candida krusei* MTCC9215
Streptomyces rochei	Silver	Extracellular	–	*Pseudomonas aeruginosa*, *Escherichia coli*, *Klebsiella pneumoniae*, *Enterobactor faecalis*, *Staphylococcus aureus*
Streptomyces sp.	Silver	–	–	*Staphylococcus aureus*, *Staphylococcus epidermidis*, *Escherichia coli*, *Salmonella typhi*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, *Proteus vulgaris*
Streptomyces sp. BDUKAS10	Silver	Extracellular	21–48/ spherical	*Pseudomonas aeruginosa* MTCC 1688, *Bacillus cereus* MTCC1272, *Staphylococcus aureus* MTCC96
Streptomyces sp. VITBT7	Silver	Extracellular	20–70/ Spherical	*Staphylococcus aureus* MTCC739, *Klebsiella pneumoniae* ATCC700603, *Pseudomonas aeruginosa* MTCC424, *Bacillus cereus* MTCC1168, *Escherichia coli* ATCC25922 *Aspergillus niger* MTCC1344, *Candida albicans* MTCC227, *Aspergillus fumigatus* MTCC3002, *Aspergillus flavus* MTCC1973
Streptomyces sp. I,	Silver	Extracellular/ intracellular	65–80/ Spherical	*Staphylococcus aureus*,
Streptomyces sp. II,				*Escherichia coli*,
Rhodococcus sp.				*Pseudomonas aeruginosa*, *Klebsiella pneumoniae,* *Proteus vulgaris*
Streptomyces aureofaciens MTCC 356	Silver	Extracellular	–	*Staphylococcus aureus* ATCC29737, *Bacillus subtilis* ATCC6633 *Escherichia coli* ATCC10536, *Pseudomonas aeruginosa* NCIM2945

(continued)

Table 4.1 (continued)

Actinomycetes used for synthesis	Type of NPs	Intracellular/ extracellular	Size (nm)/ shape	Target organisms
Streptomyces sp. JF741876	Silver	Extracellular	80–100	*Staphylococcus aureus* MTCC 3160, *Escherichia coli* MTCC1302 *Trichophyton rubrum,* *Trichophyton tonsurans*
Streptomycetes viridogens HM10	Gold	Intracellular	18–20/ Spherical, rod	*Staphylococcus aureus,* *Escherichia coli*
Streptomyces sp.	Zinc	Extracellular	Spherical	*Staphylococcus aureus, Escherichia coli, Salmonella* sp.,
Streptomyces sp.	Zinc Copper	Extracellular/ Intracellular	–	*Escherichia coli* ATCC8739, *Staphylococcus aureus* ATCC6538*, Aspergillus niger*

Reproduced from Golinska et al. (2014) with some modification

4.3 Role of Nanotechnology and Its Implications on the Food World

4.3.1 Packaging and Delivery of Food via "Encapsulation"

The process of packing the substances of interest in nanosized carriers is termed as nanoencapsulation. This process involves different techniques for the generation of the nanoencapsulated particles, such as nanocomposites, nanoemulsification, and nanorestructuration, and leads to the final completed functionality of the nanoparticles with controlled release of the core. The safeguarding of the payload—in this case the bioactive compounds, such as vitamins, antioxidants, and other biomolecules for the production of the functional food with increased stability and higher functionality. The development of techniques that lead to the generation of the nanocapsules have been well studied (Quintanilla-Carvajal et al. 2010; Camacho Díaz 2013).

The advancement of encapsulation of nutrient-rich substance loaded with healthy compounds includes vitamins and antioxidants. The nanoparticles are encapsulated/ or packaged via the process of encapsulation. Encapsulated substances survive the gastrointestinal framework to convey their payload at a specific site, along these lines amplifying the useful impact. Because of non-strong and semi-strong sustenances, it is additionally crucial to diminish the lattice size to permit their fuse without influencing nourishment-tangible qualities (López-Rubio et al. 2012; Orive et al. 2015; Pedraz et al. 2015). Certain naturally found substances, such as the omega-3 fatty acids found in oily fish, plants, and some seed oils are the latest addition to the list of cardiovascular risk reduction effective foods list (Dehmer et al. 1988; Kaushik et al. 2014; Lane and Derbyshire 2015).

The discharge or release of the compounds from the oversized encapsulated particles are carried in more and overextended or sustained intervals, whereas the particle size reduction introduces several factors that led to increase adhesive force from the particles, therefore heightened the G1 period, and finally resulted in the increased bioavailability of compound of interest (Chen et al. 2006; Kumari and Yadav 2014).

4.3.2 Probiotics Delivery

The term probiotics is used to define "viable organisms which when administered in adequate amount (10^6–10^7 CFU/g) to the human host confer health benefits." Releasing probiotics through ingestion of practical nourishment has been proposed to be connected with a few medical advantages, including regulation of the gastrointestinal tract, incitement of the safe framework, diminishment of serum cholesterol levels, alleviation of lactose prejudice and touchy gut disorder symptomatology, aversion of cardiovascular malady, and a few types of tumours (Chong 2014). Probiotics are for the most part characterized as live blends of bacterial species and can be joined in sustenances, such as yoghurts, yogurt-sort aged milk, cheddar, puddings, and natural product-based beverages. Typified types of fixings accomplish longer timeframe of realistic usability of the item. Nanoencapsulation is attractive to create planner probiotic bacterial arrangements targeted to specific parts of the gastrointestinal tract where they are associated with particular receptors. These nanoencapsulated creator probiotic bacterial arrangements may go about as all over again immunizations, with the capacity of tweaking insusceptible reactions (Vidhyalakshmi et al. 2009; Haghshenas et al. 2015; Wang et al. 2015).

The microbial communities can be easily affected, resulting in changes in intestinal microbiome and the microbial metabolome by both genetic and the surrounding ecological physical and chemical factors. These factors include the consumption of antibiotics, which can affect the normal microbial microflora of intestines of the concerned animals. "Probiotics" generally is related to the preventive medicine rather than the therapeutic process and can be placed opposite to "Antibiotics" (Nami et al. 2015). Encapsulation of probiotic cells in low moisture (spray or freeze dried matrices), cross-linked, or self-assembled biopolymer microparticulates and recently immobilisation in single or composite biopolymer substrates, e.g., edible films, are currently the commonest strategies to surpass the obstacles relating to probiotics lethality due to food processing (Anal and Singh 2007; Kailasapathy 2015).

The natural and organic substances taken as food consist of the active components that are packaged properly and safeguard the packaged active materials until delivered to the targeted human organs. The process of microencapsulation has been utilized to release safely the active components in the processed foods. The encapsulation efficiency has been stabilized against the entrapped nutrients from the food from its bioavailability. The encapsulated components along with the bioactive nutrients are required for improved health and to avoid future illnesses (Onwulata 2012).

4.3.3 Polymer-Based Nanoparticles

The controlled and targeted release of the functional compounds from the polymeric-based nanoparticles (Zigoneanu et al. 2008; Zohri et al. 2009; Stark et al. 2015; Prasad et al. 2017a). For example, the PLGA-NPs increase the maximal plasma concentration ($C_{\max}$) and area under the time-concentration curve among the experimental rats by almost 54.5- and 77.6-fold, respectively, thereby resulting in the amassing of the tissue at the mesenteric fat and the spleen, whereas compared with micellized lutein, PLGA-NPs loaded lutein drastically changed $C_{\max}$ by 15.6-fold and in some selected tissues ≥3.8-fold (Kamil et al. 2016).

4.3.4 Emulsions

The process of sterilization of food packaging and bundling of food storage has been carried by the nanoemulsions. A common example is that nanomicellar-based products have claimed to consist of the compound glycerine, which removes the accumulation of the harmful chemicals like pesticides. The role of nanoemulsions has resulted in good consideration from the sustenance business and therefore increased profits. This process also results in the improvement of the flavours to the beverages affecting the product appearances. They have proven to be more effective against a number of bacterial and fungal pathogens, such as Gram-negative bacteria (Reineccius 2001; Silva et al. 2012).

The food procurement and packaging sector have been increasingly utilizing food-grade nanoemulsions due to their physicochemical properties, which are in proportional to increased, efficient encapsulation, solubilisation of the active compounds, and sustained and targeted delivery of the entrapped active compounds. The process of the nanoemulsions is listed as important vehicles for the long-term release of bioactive compounds, which can be enumerated as the safest way to deliver (Prasad et al. 2017b). It may be due to smaller size at range of nanometres, increased surface area. It is a perfect technique for the fabrication of the bioactive compounds at the nanoscale (Karthik et al. 2015). The process of nanoemulsions usage has been studied in the food processing and packaging industry, which has been studied in detail (Ozturk et al. 2015a; Xue et al. 2015). The improvement in the concentration of the payload compound causes better protection for the food. The increment in concentration of the bioactive compounds that caused higher cellular-based antioxidant effects and the cell proliferation among the seed oil and some infusion of crude plant material have been gained considerable positivity and importance as traditional techniques (Gumus et al. 2015). Certain important attributes have been considered for the packaging material used if it is oil-based, which effects the lipid digestion and the vitamin bioavailability of the discharge or release of active compounds from the lipid droplets and their solubilisation in mixed micelles. These nanoemulsions are prepared using the log chain triglycerides, which are isolated from the corn or fish oil and are most promising at the providing the vitamin release both in vitro and in vivo (Ozturk et al. 2015b). Therefore, the chemical and physical properties of the bioactive components, such as encapsulated fish oil and sugar beet pectin, must be added as the another substitute for the milk proteins and Arabic gum for food ingredients encapsulation (IRé 1998; Reineccius 2001; Gharsallaoui et al. 2007).

4.4 Conclusions

Nanotechnology can possibly enhance food, making them more delicious and healthier to create newer nourishment items and newer nourishment bundling in addition to stockpiling. Again, various protocols are now at a rudimentary phase and are gone for costly markets items at any rate in a short period. Fruitful utilizations of nanotechnology to nourishments are restricted. Nanotechnology and its applications can be used for upgrading nourishment flavour and surface, to decrease fat substance, or to typify supplements, for example, vitamins, to guarantee they do not debase amid an item's timespan of usability. Notwithstanding these, nanoparticles and microparticles could be utilized to make bundling that stabilizes the item inside more edible for longer. Insightful sustenance bundling and consolidating nanosensors could furnish shoppers with data on the condition of the nourishment inside. Nourishment bundles are installed with nanoparticles that alert buyers when an item is no longer safe to be consumed. These sensors can caution prior to sustenance becomes spoiled or could advise the precise wholesome status present in the substance. Nanotechnology is going to convert and modify the creation for the whole bundling industry. Nourishment nanotechnology advancement offers vital difficulties for both government and industrial modules. The sustenance preparing industries must guarantee shopper certainty and acknowledgment of nanofoods. Administrative groups, for example, the U.S. Food and Drug Administration, should create direction concerning the parameters to be followed in assessing security for sustenance, nourishment bundling, and supplement employments of nanoparticles with novel properties.

Undeniably, the marine Actinobacteria-based nanoparticles manufacture has a colossal impact on bringing down generation expense, keeping away from natural contamination, decreasing physiological lethality, and improving organic similarity. Subsequently, amalgamation with common items as crude material as a rule has a positive advancing impact on the aforementioned issues. Approximately 70% of normal items are confined from marine Actinobacteria. It is low in cost, effectively accessible, and a large portion of them cannot be blended by synthetic systems. The characteristic items from marine Actinobacteria had a wide mixture of use, yet to date marine Actinobacteria-based nanoparticles was not completely investigated in the purpose of nourishment industry. In light of the above applications, without a doubt, marine Actinobacteria nanofactories in the food industry will be beneficial. In the future, marine Actinobacteria nanofactories in the food industry should be researched and illuminated critically.

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Revolutionizing the Food Supply Chain in the USA: The Impact of Nanotechnology

5

Neslihan Aydogan-Duda

Abstract

This chapter provides with evidence to the large-scale impact of nanotechnology on the food industry in the USA. The existing reservations on the implementation side along with the extent of productivity improvements and the possible proliferation of the new products and processes are discussed. A prescription to this dilemma, i.e., the safety concerns that might affect the population health versus the economic gains from the application of nanotechnology, is offered. Unlike the development of the Internet and its recently recognized impacts on a nation's security and the recent regulation efforts, this multifaceted industry and its implications are argued to be best regulated on a piecemeal basis where the technology implementation and regulation are developed simultaneously.

Keywords

The food industry • Nanotechnology • Regulation • Supply chain

5.1 Introduction

Nanotechnology can be defined as an engineering matter at its molecular level. As such this technology has the potential to transform several industries due to its wide range of implications. One such industry is the food industry. Specifically, ranging from food processing to food packaging to nutraceuticals delivery to safety and sensing to functional food delivery, each step of the food supply chain embeds great potential to benefit from the implications of nanotechnology with increased efficiency and safety (Prasad et al. 2017). As it is described on environmentalleader.

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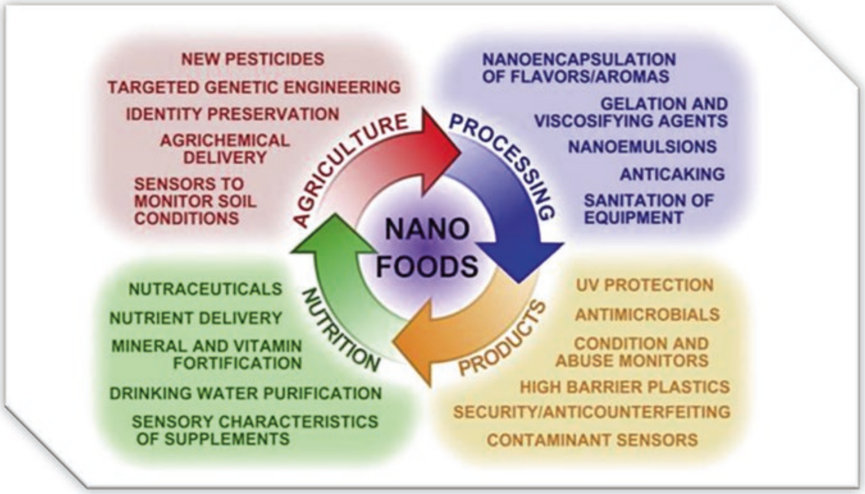

Fig. 5.1 Source: How will nanotechnology affect agricultural supply chains? (2014)

com, some of these benefits can be listed as the following (a summary of the below can be viewed in Fig. 5.1):

- The development of a contamination sensor: This would involve flashing a light to reveal the presence of *E. coli*.
- The development of antimicrobial packaging: This would involve developing edible food films made with cinnamon or oregano oil or nanoparticles of zinc, calcium, and other materials that kill bacteria.
- The development of improved food storage: This would involve developing nano-enhanced barriers that keep oxygen-sensitive foods fresher.
- The development of enhanced nutrient delivery: This would involve nano-encapsulating which improves the solubility of vitamins, antioxidants, healthy omega oils, and other “nutraceuticals.”
- The development of green packaging: This would involve developing nano-fibers made from lobster shells or organic corn which are both antimicrobial and biodegradable.
- The development of pesticide reduction: This would involve a cloth saturated with nano-fibers which slowly releases pesticides, eliminating the need for additional spraying and reducing chemical leakage into the water supply.
- The development of tracking tracing and brand protection: Nanobarcodes can be created to tag individual products and trace outbreaks.
- Improving texture: Food spread ability and stability can be improved with nano-sized crystals and lipids for better low-fat foods.
- Improving flavor: This would involve tricking the tongue with bitter blockers or sweet and salty enhancers.

- Identification and elimination of bacteria: Nano-carbohydrate particles bind with bacteria so they can be detected and eliminated.

As it is described by Sastry et al. (2012), the above are possible due to the greater penetrability, reactivity, surface area, and quantum properties of nanomaterials which enable producers to employ less material. Furthermore, nanomaterials also allow for entirely new or more efficient chemical and physical reactions. In summary, the application of nanomaterials is relevant to each phase of food processing, production, marketing, and sales by not only reducing costs at each phase but also improving the processes and products themselves. In essence, these changes appeal both to the producers and the consumers. Some of these applications are already in place despite a series of concerns related to the impact of nanomaterials on the environment and human health.

In this chapter, our goal is to describe some of the advances that already took place in the food industry in the USA and the impact of these developments on the food supply chain. In addition, we propose the necessity of further applications that can impact the food industry substantially and can produce less issue in terms of their regulation.

5.2 Nanotechnology in Supply Chain Efficiency

As it is indicated in Lua and Bowles (2014), smart sensors with "intelligence" capabilities are expected to revolutionize the agriculture supply chain management in the near future (5–8 years). To be specific authors mention that smart sensing is mostly applicable to microelectromechanical systems (MEMS) technology, which integrates mechanical elements, sensor material, and electronics on a common silicon chip through microfabrication techniques. Furthermore, authors claim that the initial work by the Intermec Technologies Corp. to use MEMS-based technology in supply chain data collection equipment has confirmed it is possible to produce laser data collection scanners that are significantly faster, smaller, lighter, and more efficient than today's legacy scanners (Anon 2005). Subsequent tests confirm that MEMS-based laser scanners are able to read bar codes up to 40 times faster with more accuracy, a massive advancement over existing scanner technologies that highlight the need for even better information management technologies to be developed before improvements to supply chain visibility can be fully realized (Anon 2005). Later developments have therefore moved into a field related to smart sensing-smart decision analytics. This is based on the capture, analysis, and reporting of the data obtained from the smart sensors (Tien 2011). Due to the superiority of nanotechnology, it will soon be possible to embed the present technology in the SCM to improve the efficiency of the supply chain.

In addition, based on the nature of the nanomaterials, they have several impacts at all the stages of the food supply changes which we analyze below.

5.3 The Financial Implications of Nanomaterials in the US Agri-Food Sector

Even though the technology has been available for a long while, applications of nanomaterials throughout the food supply chain are rather new. Such is due to the human health concerns and environmental risks and the lack of a clear regulatory framework. As it is indicated in Halvorson et al. (2014), the Department of Agriculture in the USA forecasted the international market of nanotechnology as per the food sector to be around 1 million dollars. As it is indicated in Sabourin and Ayande (2015), nanotechnology has in fact have the potential to make the food industry greener and induce competition. Indeed, currently, the authors note that the growth rate of the industry is 25% per year which is equivalent to 1.08 billion American dollars. Furthermore, Sabourin and Ayande (2015) argue that nanotechnology can transform this sector with the potential to increase the agricultural productivity, food security, and economic growth by at least 30% which is on average 0.9 trillion dollars.

In reality despite the concerns on the safety-related matters along the food supply chain, many farmers are taking advantage of nanotechnology and its impacts on productivity. For example, Ditta (2012) mentions a Californian vineyard Pickberry which employed Accenture to provide with a Wi-Fi system for the employment of nanosensors to receive the best grapes. Nanosensors provide detailed information on crop and soil conditions enabling the farmers to make the most effective and efficient decisions. The expected and observed impacts of nanotechnology are so vast and substantial that currently the USA leads the world with a 4-year plan where 3.7 billion dollars are invested via its National Nanotechnology Initiative (Schiefer and Hartmann 2013; Banterle et al. 2014). Further to support this, recent study from the Helmut Kaiser Consultancy predicts that the nano-food market will surge from 2.6 billion American dollars to 20.4 billion American dollars by 2018 (Brenes et al. 2014). Another supportive data is provided by the Business Communications Company which shows that the market for the nanotechnology shows that the market for nanotechnology in this sector was 7.6 billion American dollars and is expected to be 1 trillion American dollars in 2020 (BCC 2014).

Figure 5.2 provides a picture of the nanotechnology possibilities in the agricultural business, trends that are likely to shape the applications of nanomaterials in the agricultural sector, and possible strategies for companies in this sector and the growth possibilities where the USA is depicted with the largest expected economic growth implicated by nanomaterials.

5.4 Examples of Foods, Food Packaging, and Agriculture Products that Contain Nanomaterials

Currently as it is listed in Table 5.1, the applications of nanomaterials in terms of food products are rather restricted. As it is explained in prior, this is due to the somewhat unknown and understudied implications of nanoparticles if they happen to

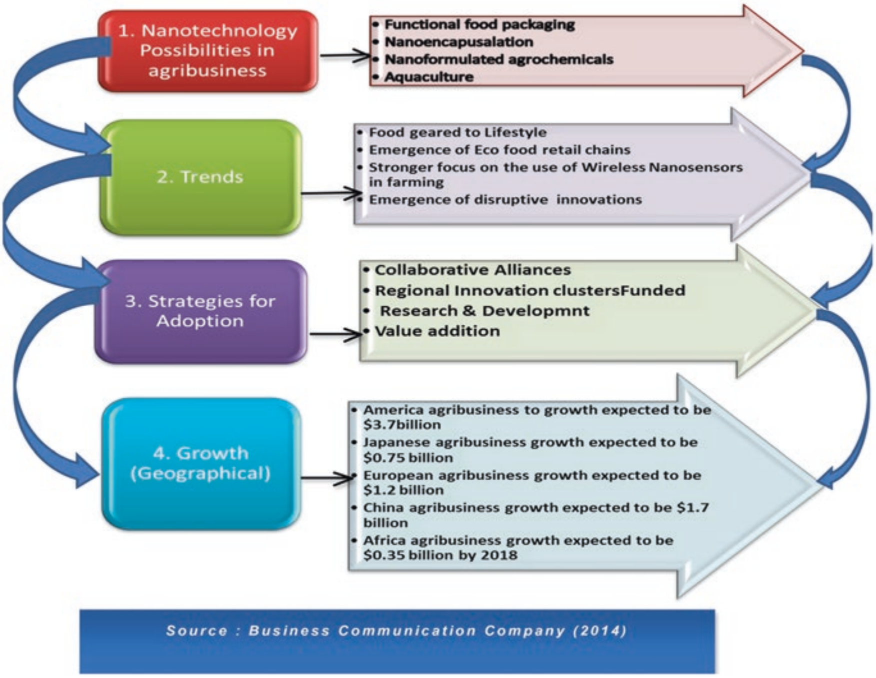

Fig. 5.2 Nanotechnology and its impacts on the food supply chain

contaminate the environment and or humans who are exposed to such. In addition, a clear regulatory framework is missing that further stalls the investment efforts in this highly lucrative field. One additional and a rather imperative lie in educating the farmers as per the extremely viable financial consequences of applying nanomaterials to agricultural processes.

We highly recommend that in industries such as the US agricultural sector where genetic modification is exercised and largely accepted, the development activities as well as the widespread applications of nanomaterials in the food sector should develop simultaneously with the regulatory framework. The regulatory framework can feed from what is being researched in the sector and such can help a competitive edge to be developed by the US investors in a more efficient way.

Nanotechnology in its broad sense can lead to some misunderstandings as to its implications on individuals and the environment. However, as we clearly explained above, not following the research and delaying the development of a regulatory framework could mean a loss of billions of dollars just for the food industry alone in the USA. This technology is rather different than the others: such as the development of the Internet which we have been observing a gradual application of the regulatory rules. The reality of the matter calls for more sophisticated implications and a more sophisticated technology that has an ability to increase the value added of an entire supply chain in a variety of industries. The food sector is one where the

Table 5.1 Current and future applications of nanotechnology in the food industry

Type of product	Product name and manufacturer	Nano content	Purpose
Beverage	Oat chocolate and oat vanilla nutritional drink mixes; Toddler Health	300 nm particles of iron (SunActive Fe)	Nano-sized iron particles have increased reactivity and bioavailability
Food additive	Aquasol preservative; AquaNova	Nanoscale micelle (capsule) of lipophilic or water insoluble substances	Nano-encapsulation increases absorption of nutritional additives, increases effectiveness of preservatives and food processing aids. Used in a wide range of foods and beverages
Food additive	Bioral™ omega-3 nanocochleates; BioDelivery Sciences International	Nanocochleates as small as 50 nm	Effective means for the addition of highly bioavailable omega-3 fatty acids to cakes, muffins. pasta, soups, cookies, cereals, chips, and confectionery
Food additive	Synthetic lycopene; BASF	LycoVit 10% (<200 nm synthetic lycopene)	Bright red color and potent antioxidant. Sold for use in health supplements, soft drinks. juices, margarine, breakfast cereals, instant soups, salad dressings, yoghurt, crackers, etc.
Food contact material	Nano-silver cutting board; A-Do Global	Nanoparticles of silver	99.9% antibacterial
Food contact material	Antibacterial kitchenware; Nano Care Technology/NCT	Nanoparticles of silver	Ladles, egg flips, serving spoons, etc., have increased antibacterial properties
Food packaging	Food packaging Durethan® KU 2-2601 plastic wrapping; Bayer	Nanoparticles of silica in a polymer-based nanocomposite	Nanoparticles of silica in the plastic prevent the penetration of oxygen and gas of the wrapping, extending the product's shelf life. To wrap meat, cheese, long-life juice, etc.
Food packaging	PrimoMaxx; Syngenta	100 nm particle size emulsion	Very small particle size means mixes completely with water and does not settle out in a spray tank

Source: Kirdar (2015)

value added can be expressed in billions of dollars, and as such any country which has such a large agricultural sector as the USA, informing, educating, researching, developing, and regulating need to be executed all at the same time.

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6 Nanotechnology Applications in Food Packaging Industry

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Abstract

Nanotechnology, which uses substances on an atomic, molecular, and even supramolecular scale, is cooperating with biotechnology in stable and flexible packing business. In accordance with the recent market polls, it is obvious that the influence of nanotechnology on food and beverage packaging manufacturing has been substantially increasing. Nanotechnology provides scientists with the opportunity to modify the structure of materials on the nanoscale. Scientists may produce the new design of molecules to achieve certain purposes. Nanotechnology, which represents the discipline of very small materials, is ready to play a major role in food manufacturing and packaging. The freshness of food can be observed or shown by people, or they can demonstrate whether thawing of the frozen food has taken place in the course of its storing or conveyance. Nanostructured materials are used as oxygen hunters, antimicrobial thin films, and gas-permeable composites. At the same time, nanocomposite films may be employed for the purpose of removing dirty air, for example, carbon dioxide from the package. Nanoclay is used most frequently for acquiring barrier coatings. The exfoliation of the functionalized and nonfunctionalized montmorillonite plates is performed in order to acquire good resistance to water and oxygen passing throughout the package film. In case radiation curing technologies are associated with nanostructured polymers, it is possible to produce strong and extremely robust films. Developments in the food and beverage industry are at a very early stage and are currently being shaped by advancements in other fields, most specifically the pharmaceutical industry. Currently, the major uses of nanotechnology in the food and beverage sector are in packaging and in health/nutraceutical supplements,

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and it is anticipated that its use will not only upsurge within these sectors in the near future but will also grow into other areas including ingredient functionality, emulsions, and sensors.

Keywords
Nanotechnology • Food packaging • Nanoparticles • Nanocomposite films • Food industry

6.1 Introduction

The term "nanotechnologies, nanotech for short," is perhaps a more correct term to use nowadays, since there is such a wide range of diverse nanotechnology applications. Nanotechnologies are crossing many technology boundaries as scientists from various disciplines including chemistry, physics, and other pure sciences such as medicine, materials, sensors, and food bring their studies together in an interactive way. Nanotech represents the creation and utilization of useful structures which are produced on the atomic or molecular scale and have minimum one typical measure, which is determined in nanometers. Their dimensions permit them to display innovative and considerably enhanced chemical, physical, and biological features just because of their size. Nanoscience and nanotechnology are rapidly developing since they take place among the most imperative study and application areas. Nanotechnology is an area of applied sciences and technologies because it controls the matter on the atomic and molecular scale, at the dimension less than 100 nm (Prasad et al. 2014, 2016; Aziz et al. 2015).

Nanotech can provide us with a never-before-known understanding of materials and devices and will most probably have an impact on many areas. Utilizing structures at the nanoscale as an adjustable physical variable may significantly enhance the performance range of the current materials and chemicals. This technology has numerous applications largely in electronic, computer, material, textile, and drug industries in addition to the potential food and agricultural applications (Prasad 2014; Prasad et al. 2014). Nanotechnology, which represents the discipline of highly small materials, is ready to have a major effect in the area of food manufacturing and packaging. Methods including sun-drying, salting, fermenting, steaming, roasting, oven baking, smoking, curing, bottling, pickling, jellying, canning, irradiation and carbonation of food, and also the usage of artificial or chemical preserving agents are the methods of preservation that have been ordinarily practiced by people on a daily basis (Pradhan et al. 2015). Furthermore, vacuum preservation and osmotic inhibition represent methods frequently employed for the food conservation. Archaeological findings act as a proof of the application of these conservation methods and their presence since the Egyptian, Greek, and Roman times. People in the Ancient Egypt used to leave foods dry in the sun to preserve them from decomposition. In order to inhibit microbial contamination in food, the Romans used pickling. The Greeks, on the other hand, introduced jellying the food by using honey or sugar in the conservation methods (Abbas et al. 2009).

The foremost application of nanotechnology is for plastic and paperboard packaging due to its poor barrier properties. The utilization of nanotechnology in packaging offers light weighting opportunities to support sustainability and cost cutting measures. A significant increase has been observed in the production and usage of plastics in countries all around the world in the recent 20 years (Avella et al. 2005). Under the conditions of aggressive competition in the market nowadays, a novel leading edge technology is crucial for maintaining leading positions in the food and food processing sector. The future is going to be shaped by innovative products and novel process techniques, for the purpose of improving the product performance, extending the shelf life of products to keep them fresh, and enhancing the security and quality of food products. Worldwide statistics show that 86% of sea turtle species, 44% of seabird species, and 43% of marine mammal species are vulnerable to the marine plastic rubbish they ingest (Agnieszka et al. 2011). Since 1950, an annual increase from 0.5 to 260 million tons has been observed in the production of plastics.

A number of innovative nanotechnology applications, such as the usage of nanoparticles that include micelles, nanoemulsions, liposomes, cubosomes, and biopolymeric nanoparticles, along with the advancement of nanosensors intended for securing the food safety, have emerged in the food industry (Sozer and Kokini 2009). At the nanoscale, materials can introduce diverse electronic features, therefore, affecting their catalytic, optical, and other reactive characteristics (Kahn 2006; Prasad et al. 2016). Nanotechnology studies have rapidly increased during the past 10 years, and by now, there are many businesses that have dedicated themselves to the creation of the novel forms of nanosized materials, with projected applications involving energy generation, molecular computing, medical therapeutics and diagnostics, and structural materials. There is the first level of association at the nanoscale in every biological and man-made system. Similarly to nature, it is possible to pull molecules together into functional objects by employing nanotechnological methods, along a few length scales, and to take objects apart into molecules (Roco 2003). In 2008, nanotechnologies claimed more than $15 billion in the money intended for worldwide studies and development (including both the public and private sectors), and more than 400,000 researchers all around the world were employed (Roco et al. 2011).

It is estimated that nanotechnologies will affect minimum $3 trillion in the worldwide economy by 2020, and global nanotechnology industries will need minimum six million employees for the purpose of their maintaining by the end of 10 years (Roco et al. 2011; Wesley et al. 2014). The utilization of protective coatings and appropriate packaging techniques in the food industry has become an issue of peculiar interest due to their potential to improve the shelf life of various food products (Hernandez et al. 2000; Ahvenainen 2003). The correct choice of materials and packaging techniques will allow maintaining the freshness and quality of products over the period necessary to market and consume them (Brown 1992). Searching for innovative bio-based wrapping materials, for example, edible and biodegradable films from sustainable resources, has been stimulated by a great endeavor to prolong the shelf life and improve the food quality along with decreasing packaging waste (Tharanathan 2003).

On the other hand, developments in the studies on nanotechnology applications in food and food-related products have just started to be observed in spite of the improved marketing achievements in nanotechnologies (Chau et al. 2007). Cooking oils containing nutraceuticals within nanocapsules, nanoencapsulated flavor enhancers, and nanoparticles which can facilitate selective binding and removal of undesired chemicals from the food can be shown as the representative examples of the nanotechnology usage in food products. Concerns about the potential labeling of food products and consumer health issues constitute the principal causes of the late integration of food into the industry of nanotechnologies. The utilization of food packaging represents a socioeconomic sign of the improved capability of the general population to spend or the gross domestic product along with regional (rural versus urban) food accessibility. Food safety and quality have constantly remained a matter of great worry. With the idea of a healthy nation at the top of the priority list, scientists have been striving to discover advanced technologies for the purpose of improving food safety and quality. The introduction of nanotechnologies in the food industry has made the design and development of innovative food, which has higher thermal stability, solubility, and oral bioavailability characteristics, possible (Pradhan et al. 2015).

At the present time, new technologies are shifting the global economy to facilitate technological innovations governing the appearance of the economy and markets, and they will cause the creation of new business models. As a consequence, we must plan from now on, and with the technological novelty related to nanotechnologies, it is possible for us to accomplish the purposes, and the use of the abovementioned technologies in the paper and packaging sector can result in more considerable and smart packaging. There is a potential of nanotechnologies to influence various characteristics of food systems. Packaging systems, food security, and innovative materials intended for pathogen recognition can be presented as the examples of the significant relation of nanotechnology with food science and engineering (Fig. 6.1). Food processing, the development of innovative functional foods, conveyance and the controlled release of bioactive materials, the detection of pathogens, and prolonging the shelf life by the enhancement of new packaging materials are some of the prospective food applications of nanotechnology.

Therefore, adding of bioactive materials that provide health welfares into foods is increasingly performed for the purpose of treating or precluding illnesses. On the other hand, obstructions are present in the production, storage, and dissemination of foods with integrated bioactive constituents. Because of the diversity of conventional meat products, the obstacles are probably very extensive in the meat sector. The low level of bioavailability of bioactive elements when incorporated in meat products, primarily due to comparatively raised levels of fats, proteins, and minerals, constitutes a substantial difficulty. Thus, it has been endeavored to make adaptations to the manufacturing of meat products. However, the abovementioned adaptations have frequently caused undesired impacts, for example, a bad organoleptic quality, reduced ability to keep water, as well as weak resistance to microbial

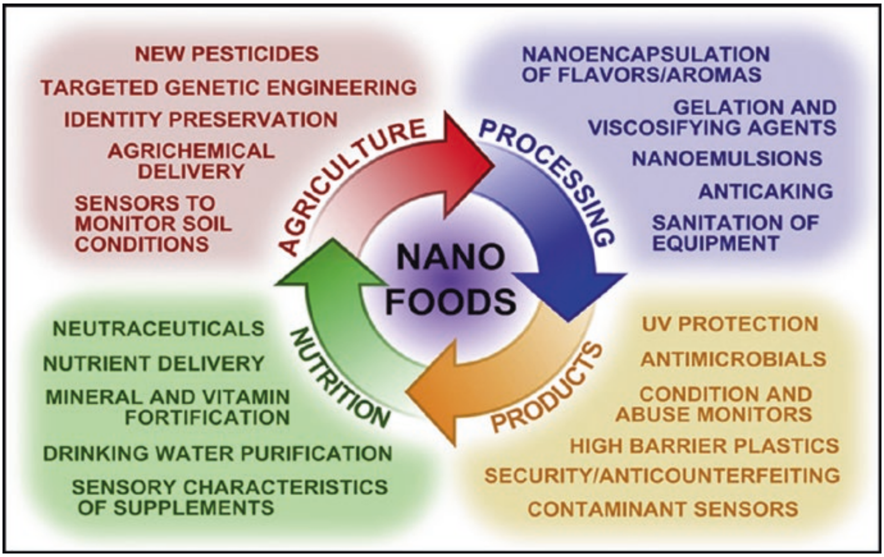


Fig. 6.1 Nanotechnology is employed in all fields of food science from agriculture to food processing, safety, and packaging to nutrition and neutraceuticals

development (Weiss et al. 2010). Consequently, the meat sector preconditions the application and support of an innovation agenda to deal with these difficulties and eventually increase the quality of products (Troy and Kerry 2010). Therefore, nanotechnology takes place among these process-based advancements with a substantial effect on the food sector (Linton and Walsh 2008).

One division of innovation is being recent and novel. Being recent can range from incremental changes to radical innovations. Incremental innovation denotes changes which generate current products, while radical innovation refers to completely novel products and services. Acknowledging the significance of innovation for the growth of countries, the fundamental technological novelties presented by nanopapers in various phases of fabricating paper, which involve the preparation of stocks; the usage of approved supplements, fillers, and pigments, and the use of retention, calendar, and phases of manufacturing conductive paper, porous nanopaper, and layer-by-layer self-assembly, are discussed in the present chapter. According to the study findings, in case the jungle-related merchandises do not accept thorough advances, they will substantially lose their market share in the following years. With the implementations of radical innovations in the packaging sector, novel value-added products and materials can be produced. On the other hand, the implementation of nanotechnologies in the abovementioned sector may be expensive. Therefore, it can be realized by cooperating with other sectors to ensure the use of nanotechnologies at maximum (Ahvenainen 2003; Wesley et al. 2014). As a result, all manufacturing processes can adopt the abovementioned technology, which brings about the mass production of low-cost, simple, and flexible papers and distinctive characteristics, including facility at shape, form, easy conveyance, low weight, recovery and recycle marketing capabilities, and sealing. Enhancing the strength of wrappers without decreasing their performance enriches the quality and the value added of packaging (Kachlami et al. 2012).

It is necessary to evaluate the traditional, mechanical, chemical, and semichemical methods in the paper and packaging sector. As a major development, nanopapers produced with nanotechnologies may enhance practical characteristics and lead to growth in the added value of paper products in addition to affecting the market growth of papers. Paper represents an inexpensive, recoverable, and yet more environmentally friendly material among the four types of packaging materials, being metal, plastic, paper, and glass. Consequently, its growth and expansion rate has also been higher (Stewart et al. 2002). It is possible to produce nanomaterials by using two general methods, top-down and bottom-up. The first one of these methods, known as the top-down method, is mainly utilized to process materials of inorganic nature by using old-fashioned techniques, for example, grinding, milling, sieving, and chemical reactions (Cockburn et al. 2012). Homogenization can be shown as an example of a top-down approach in which pressure is employed for decreasing the dimension of constituents, for example, fat globules. In milling, the dimensions of materials are decreased in a mechanical way for the purpose of increasing their functionality (Cushen et al. 2012). On the other hand, the bottom-up method encompasses the gathering of smaller-size molecules by means of self-organization, bringing about the creation of supramolecular structures with unusual performances (Cockburn et al. 2012). To illustrate the bottom-up method, layer-by-layer deposition and solvent evaporation can be presented (Cushen et al. 2012). The abovementioned techniques are usually utilized in food practices by means of elements, for example, phospholipids (Cockburn et al. 2012).

There are differences between the characteristics of nanomaterials, including physical, chemical, and biological features, and the characteristics of individual atoms and molecules or bulk matter. To take the essential characteristics of materials that include their magnetic characteristics, melting temperature, charge capacity, and color without altering the chemical compositions of materials under control is possible through the formation of nanoparticles. It is optimal to utilize nanoparticles and nanolayers in polymeric materials due to their extremely high surface to volume and aspect rates. The abovementioned configurations bring the most outstanding characteristics of all elements together to have boosted mechanical and superconducting features for cutting-edge practices. The characteristics of the individual parents of nanocomposite materials and their morphology and interfacial properties essentially determine the major characteristics of these materials. A number of nanocomposite materials may be as much as 1000 times stronger when compared to the bulk element. The overall class of nanocomposite organic and inorganic materials constitutes a rapidly developing study area (Stewart et al. 2002; Azeredo 2009). Composite materials with micron-scale ferroelectric ceramic particles taking the role of the filler in liquid crystal polymer, fluoropolymer, or thermoplastic polymer matrices do not bear perfect processing features and are challenging to form into the thin uniform films employed in numerous microelectronics practices. In this case, it is required to employ nanocomposite materials with a rich variety of materials brought together at the nanoscale.

Nanocomposite films may be utilized for the removal of dirty air, for example, carbon dioxide out from the package. For instance, for acquiring barrier coatings, nanoclay is utilized most frequently (Tharanathan 2003). The exfoliation of the functionalized and nonfunctionalized montmorillonite plates is performed for the purpose of acquiring good resistance to oxygen and water passing throughout the package film. It is possible to acquire strong and extremely durable films in case radiation curing techniques are associated with nanostructured polymers. Swift curing capability, solvent and abrasion resistance, and outstanding process control constitute additional benefits of ultraviolet (UV)/electron beam (EB) methods. A number of metal oxides and minerals may be employed for obtaining nanostructured UV curing films. The sol-gel mechanism has been employed to investigate urethane, epoxy, and polyester acrylates. Studies have been conducted to examine nanoscale particles comprising composites considering their scratch resistance, applicability, and elasticity (Bharadwaj et al. 2002). In this chapter, it has been focused on various characteristics of nanotechnologies linked to the food quality and the advancement of smart foods and food packaging materials, in addition to the usage of nanosensors in order to determine contamination by microbes and pesticides. The implications of food nanotechnology will also be reviewed, and it will be attempted to identify the existing problem areas in nanotechnology in terms of the possible risks nanomaterials may pose for the environment and health, in addition to regulatory aspects and view of the public.

6.2 Nanotechnology in Packaging Industry

Nanotechnology is commonly stated to be the construction and use of structures which have minimum one parameter in the nanorange (10^{-9} m). The abovementioned constructions are named nanocomposites, and they can reveal modifications in the characteristics of materials and generate innovative features and phenomena to materials. In order to attain the abovementioned changes, it is anticipated that the polymer matrix, which represents the continuous phase, and the nanofiller, which represents the discontinuous phase, will interact in a sound way. The applications of nanomaterials are presently practiced for meat and food, in general, such as the usage of nanoparticles and nanomaterials as food ingredients/additives, which are put into the food in a direct way or used as an element of the food packaging (Duncan 2011; Prasad et al. 2017). In accordance with the results of the study conducted by Chaudhry et al. (2008), the use of nanomaterials in food systems is principally observed in the production of food components using nanostructures and in conveyance systems for additives and nutrients. The study areas in meat products comprise remaking by means of reducing and revising the content of fats; reducing the quantity of phosphate, sodium, and nitrate; and the presence of prebiotics, probiotics, and other materials including walnut and seaweed. Furthermore, the enhancement of bioavailability and the creation of compounds capable of stimulating health and decreasing harmful compounds constitute the potential research fields with regard to the processing and storing of meat products (Ramachandraiah et al. 2015).

Surface engineering delivers supplementary performance to solid surfaces, includes compositions and structures which are normally not present in solids, is employed for the purpose of changing the surface characteristics of solids, and encompasses the use and plasma treatment. Moreover, surface engineering may be described as design and alteration of the surface and substrate of an engineering material together as a system, which results in economical performance which neither can achieve on its own (Bard 1994). Technologies of surface engineering may be employed to generate a number of practical features that include physical, chemical, magnetic, and mechanical features, wear resistance, and features on the desired substrate surfaces. It is possible to perform coating of nearly all kinds of materials, ceramics, metals, composites, and polymers on materials, which are similar or dissimilar (Sternitzke 1997).

Numerous engineering constituents require surfaces, which are resistant to wear or corrosion, in addition to substrates, which are hard and resistant to various impacts. It is possible to achieve the abovementioned in the best way by employing methods which modify surface characteristics but not change the characteristics of the core or bulk material considerably. There are many other characteristics of a solid surface, which may be improved by the use of thin films, plasma treatment, patterning, and nanoscale structures for packaging (Sproul 2003). If these fundamentals are applied properly, surface engineering may bring countless benefits that include lesser production costs, reduced and prolonged maintenance intervals, improved recyclability of materials, and a much less effect on the environment. The texture of food products, particularly of dairy products, can be enhanced by nanotechnology. It may also conceal the unpleasant, or strong, and unacceptable flavor and odor of a number of substances for the consumer, for example, fish oil that is currently commercialized just in the form of microencapsulated fish oil added to bread; however, there are inferences about the possibility of its use in various food products (Chaudhry et al. 2008; Cushen et al. 2012; Davarcioglu 2015).

The applications of thin film coatings on glass are aimed at reflecting, transmitting, and creating heat. The possibilities of surface engineering are infinite. For instance, besides the coatings, which are wear resistant, various kinds of coatings, specified below, are created: decorative coatings; photocatalytic thin films, for example, TiO_2, which may convert a glass surface into surface capable of self-cleaning (Mital and Manoj 2011); polymer dielectric multilayer films that may reduce water and gas permeability of a plastic surface by six orders of magnitude; and oxygen and water permeability barriers for delicate plastics, electronics, and food packaging. The food composition (Cushen et al. 2012), including fats, proteins, and carbohydrates, should be taken into account since it may influence the possible functionalities of nanomaterials used directly in food, and it is required to study it for the purpose of enhancing the functionality of products without compromising the safety and quality of food.

The decrease in decomposition constitutes one purpose of pioneering wrapping solutions. It is possible to perform manufacturing, processing, and transporting of food products in a more secure way by utilizing nanosensors in order to determine pathogens and impurity. The infusion of silver, which is a recognized antimicrobial agent, into storage vessels is performed for hindering bacterial growth and permitting the storage of food products for a prolonged time period. As a result of a case study, it was revealed that silver nanoparticles are able to reduce the 24-h growth of bacteria by over 98% (Wesley et al. 2014). An improved protection of food products against external mechanical, chemical, thermal, or microbiological impacts is ensured by the development of nanomaterials having improved mechanical and thermal characteristics. For example, nanocomposites represent nanoparticles embedded within polymers in such a way that improved characteristics, including a lighter weight and enhanced recyclability, in addition to decomposition and flavor concerns, are provided to materials. At present, nanocomposite materials are used in beer bottles, which extend the shelf life up to 6 months (Azeredo 2009).

6.2.1 Food Packaging

Packaging acts as a mute salesman since the merchandise does not demonstrate itself to consumers in a direct way, and its coverage with different forms and precise statements denotes its content and delivers essential data to the customer. Therefore, a novelty in packaging may discriminate the products from contending products and take a significant place in the marketing of goods, constituting one of the accomplishment factors of manufacturers. Nanoparticles can be used as responsive particles integrated into packaging as nanosensors, delivering the safety and quality control of products. The existence of gases, chemical contaminants, aromas, or answer alterations in environmental conditions can be sensed by nanoparticles employed as nanosensors (Azeredo 2009; Duncan 2011).

Food packaging is considered to be among the earliest commercial implementations of nanotechnology in the food business. It is reported that approximately 400–500 nanopackaging merchandises are predicted to be utilized commercially, and it is anticipated that nanotechnology will be employed in the production of 25% of all food packaging in the following 10 years. For the purpose of lengthening the shelf life, nanopackaging may also be cogitated for the release of antioxidants, antimicrobials, flavors, enzymes, and nutraceuticals (Cha and Chinnan 2004). Stimulating new nanotechnology products for food packaging is reported to be on the way, and a number of antimicrobial films have come into the market by now for the purpose of increasing the shelf life of food and especially dairy products. The innovative techniques of food packaging certainly represent the most significant advantage of nanotechnology in the food sector in the upcoming years. Corporations have been already manufacturing materials for packaging with the use of nanotechnologies, which prolong the life of food and beverages and enhance the safety of food. The foremost focus of the food business related to nanotechnology studies and advancement is food packaging and monitoring (Brody 2003, 2007).

Numerous ingredients are available for possible implementations in the processing of meat products, such as fat replacers including citrus fiber, oat fiber, carrageenan, soy protein concentrate, soy fiber, and plasma protein. Additional application areas cover the modification of the fat profile by means of the fish oil extract, flaxseed, and linseed; decreasing salt with edible seaweeds and apple pulp; decreasing nitrite by using celery and spinach juice; delivery of new antioxidants from ascorbic acid, rosemary extract, and hyssop extract; and the use of rosemary, nisin, and oregano oil as antimicrobials. The usage of nanotechnologies with the introduction of antimicrobials and antioxidants by means of nanomaterials in the meat products processed may possibly contribute to some of the applications (Ozimek et al. 2010). Nonetheless, for the performance of natural as well as modified food in the association, understanding of the constituents should be ensured for the manufacturing of nanomaterials (Augustin and Sanguansri 2009).

A group of scientists at the Norwegian Institute of Technology is employing nanotechnology in order to make very small particles in the film, and to expand the transport of a number of gases through the plastic films for the removal of the undesired carbon dioxide, which reduces the shelf life of food products. Moreover, this group of scientists is investigating whether the film can deliver barrier protection and inhibit gases, for example, oxygen and ethylene from spoiling food products (Wesley et al. 2014). Nanotechnology in packaging has a number of advantages. The first one is antibacterial: the utilization of silver nanoparticles in the form of antibacterial mediators in the packaging of food products is growing. It is usually coated on plastic packets to preclude food from going off and also integrated into food storage containers you use at home. This technology is benefited from even inside of refrigerators to preclude mold growth. The second advantage is protective coatings: a number of dissimilar nanocoatings are being studied for the purpose of keeping the food fresh and the flavor the same and also through obstructing the rays of the sun.

Considerably, lower loading levels are permitted by nanoparticles when compared to old-fashioned fillers for attaining the best functionality. The levels of adding nanofillers are commonly below 5%, which considerably influences the weight drop of nanocomposite films. The outcomes of the abovementioned dispersion process are the high aspect ratio and surface area resulting in plastics with better functionality when compared to the case when traditional fillers are used (Azeredo 2009). That is developed when protein isolate films set in with TiO_2 and SiO_2 nanoparticles for enhanced mechanical properties by solution casting (Sorrentino et al. 2007). According to the results of the tensile stress analysis, adding nanoparticles fortifies the protein isolate film, and the films of this kind may be possibly used as operational packaging materials for the purpose of increasing the safety and quality of food.

6.2.2 Nanotechnology and Food Safety

Food safety implies that it is necessary to secure all food products against any physical, chemical, biological, and radiation contamination during processing, transportation, and distribution. Thus, the implementation of nanotechnologies in the dairy and food processing, as well as packaging, has been addressed in the current study. Drastic changes have been caused by nanotechnology in the nonfood industries. Nevertheless, nanotechnology is gradually becoming popular in the dairy and food processing. Nanoparticles have a number of features, such as higher reactivity and mobility, and thus, they are likely to have a higher lethality. It is necessary to perform a complete safety evaluation of the constituents in such nanoparticles by the appropriate scientific advisory association previous to allowing their use in the dairy and food products including packaging.

It has been advised by the European Union regulations for food and food packaging that special safety standards and testing processes constitute the prerequisite of the presentation of novel nanotechnologies. Understanding of toxicity risks is ensured at a very low level because of their special characteristics, they are not evaluated as novel chemicals in accordance with various guidelines, the existing exposure and safety techniques are not appropriate for nanomaterials, and private industry studies are utilized in various safety evaluations (Cha and Chinnan 2004; Wesley et al. 2014). Furthermore, the safety evaluation of food packaging is indispensable for providing safety because of the possible migrating of nanoparticles. Moreover, along with an increase in the attention paid to nanotechnology, the advancement of nanoproducts has not maintained the prospects of customers about the safety of these products (Cushen et al. 2012). However, the efficiency of regulations in the food sector rests on the extensiveness of definitions and accountabilities of products and practices containing nanomaterials that have innovative and diverse features along with the suitable allowed levels concerning nanomaterials (Chaudhry and Castle 2011).

At present, numerous establishments participate in nanotechnology studies, rules, and instructions; the Food and Drug Administration (FDA) has delivered its view on nanotechnology. FDA sets products according to their legal classification, not the technique employed by them; it is possible that the FDA's regulatory thought of an implementation that contains a product of nanotechnology will not take place long after the primary development of the nanotechnology in question. Regulatory authority has been restricted by the FDA over a number of product groups; the authority over the usage of nanotechnology in regard to such products may have been restricted by it. For instance, no premarket endorsement of cosmetic products or their components, except for color additives, is present. The new rule delivered in 2011 on plastic food contact materials in the European Union (Commission Regulation EU No 10/2011) now comprises the usage of nanoparticles. The regulation states that the use of nanoparticles is banned unless they are precisely approved in their nanoform, and the European Food Safety Authority (EFSA) endorses that the "risk assessment of engineered nanomaterials has to be performed on a case by case basis."

The safety and quality of food can be possibly expanded by nanotechnology considerably. Presently, numerous studies are realized on the subject of nanosensors for the enhanced determination of pathogens in food systems. Furthermore, sensors capable of sensing extremely low levels of molecular indicators of decomposition and foodborne pathogens after minutes of exposure can be produced by employing the abovementioned materials. It is also anticipated that it will be possible to integrate the tongue technology into food packaging, for example, wrapping of meat products, and it will alter color in case the meat begins to go bad. Nanotechnology allows designers to modify the molecular structure of the materials used for packaging. For instance, it is possible to produce plastics which have various nanostructures to acquire different moisture and gas permeations to accommodate the demands of certain products, for example, vegetables, fruits, drinks, and wine. The intrusion of various microorganisms, for example, pathogens, may be precluded by nanostructured films and packaging materials, which can ensure food safety. Whether the food is spoiled and the nutrients it contains will be possible to determine with the food packaging with the embedded nanosensors. The weight of food packaging can be decreased, and it can be provided with fire-resistant and better mechanical and thermal properties and regulated absorption of gases with the addition of some nanoparticles into packing materials and bottles. On the other hand, the food sector and related sectors are influenced by accomplishments and findings in nanotechnology, which has an effect on significant issues ranging from the safety of food products to the molecular synthesis of novel food products and components (Chen et al. 2006).

6.2.3 Biodegradable Polymer Films for Food Packaging

Materials, of which degradation is possible by the enzymatic activity of living beings, for example, bacteria, fungi, yeasts, and the final end products of the process of degradation, including CO_2, H_2O and biomass under aerobic circumstances, and hydrocarbons, biomass, and methane under anaerobic circumstances, are expressed by the term of “biodegradable” materials.

In the course of biodegradation, primarily, the long polymer molecules are condensed to shorter and shorter lengths, and they undertake oxidation, which is expressed in the attachment of oxygen groups to the molecules of polymers. Heat (increased temperatures in landfills); UV light, which constitutes an element of sunlight; and mechanical stress, for example, wind and pressure in a landfill, initiate the abovementioned process. As a result of oxidation, molecules grow into hydrophilic, i.e., attracting water, and small to the extent that allows microorganisms to ingest them, initiating the phase of biodegradation. Biodegradation takes place in case moisture and microorganisms normally found in the surroundings are present. The plastic is entirely decomposed into the residual products of biodegradation (Fig. 6.2). As the degraded plastic is consumed by microorganisms, water, carbon dioxide, and biomass are manufactured, and they return to the natural environment through the biocycle (Peelman et al. 2013; Malathi et al. 2014).

For the general benefit, biodegradable plastics should provide benefits for the systems of waste management, in addition to the cost and performance. The present chapter deals with the possible influence of biodegradable plastics, primarily addressing packaging, and waste management by means of landfill, burning, recycling/reuse, and composting. It delivers an examination of the main life cycle

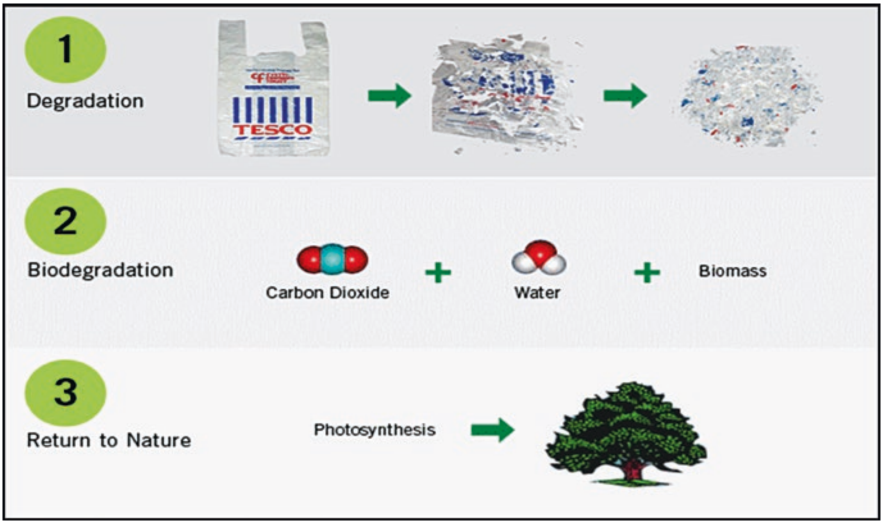


Fig. 6.2 Process of biodegradation

matters, which present judgments of the advantages of the materials in question regarding conventional and petrochemical-based equivalents. Certain examples from novel studies conducted on the subject of biodegradability in composting systems simulated under home conditions are provided. Food packaging becomes progressively imperative in the food sector, in which higher attention is paid to progress in performance, for example, handiness and portioning. In addition, a better consciousness on sustainability, the realization of which is generally possible at various levels, is ensured. At the levels of raw materials, the employment of reused materials and the utilization of sustainable resources constitute two approaches to diminishing CO_2 discharge and the reliance on fossil reserves.

Another level is the manufacturing process in which modifications, for example, aimed at a more energy-saving technology, may be carried out. An ultimate level is waste management in which hard work may be performed for the purpose of raising sustainability. Along with the recycling and reuse of the materials been in use, the production of biodegradable and/or compostable packaging aids in solving the metropolitan solid waste problem (Siracusa et al. 2008; Song et al. 2009). In the recent 10 years, the focus of interest has moved from the food, packaging and distribution sector toward the improvement and implementation of bioplastics for food packaging (Peelman et al. 2013).

6.2.4 Processing of Nanocomposites

Nanotechnology represents a comparatively innovative technology that can possibly signify the commencement of the second technical revolution. It is all about the description, production, and use of structures and materials the size of which is typically less than 100 nm (length is approximately 1–100 nm) (Duncan 2011). Although nanomaterials are considered to have at least one dimension, they may have two or three dimensions depending on the form. Nanomaterials have various forms including (I) nanoparticles, which represent the discrete entity with three dimensions; (II) nanotubes, which represent the cylindrical lattice arrangement of material; (III) fullerenes, which represent a spherical molecular structure; (IV) nanofibers that are in the nanorange with a length to diameter rate of minimum 3:1; (V) nanowhiskers, which are fine fibers in the nanorange, 5–20 nm in cross section with the length of several μm; and (VI) nanosheets, which represent materials just with one dimension in the nanorange (Baltic et al. 2013). Inorganic, as well as organic materials, can be used for the production of nanomaterials. However, they have diverse features when compared to the identical particles of a greater size. With the size reduction, changes are observed in mechanical strength, chemical reactivity, electrical and thermal conductivity, magnetism, and transparency (Ozimek et al. 2010; Cushen et al. 2012).

Composites derived from particles of nanosize ceramics and metals, the size of which is less than 100 nm, can swiftly become significantly stronger compared to the anticipated results by prevailing science models of materials. Nanoscale materials are classified into some categories:

(I) Zero dimensions: Length, breadth, and height are restricted at single point, for example, nanodots.
(II) One dimension: It has only one parameter either length or breadth or height, for example, extremely thin surface coatings.
(III) Two dimensions: It has length and breadth, for instance, nanotubes and nanowires.
(IV) Three dimensions: It has length, breadth, and height parameters, for instance, nanoparticles.

Various nanomixed and layered materials were represented by zero-dimensional core shells, one-dimensional nanowires, two-dimensional lamellar composites, and three-dimensional metal matrix composites (Sternitzke 1997). These methods of manufacturing gather the most outstanding characteristics of all elements or cause innovative and exclusive features for various progressive practices (Fig. 6.3): carbon nanotube strengthened composites, thermoplastic-based nanocomposites, thermoset-based nanocomposites, and clay-based nanocomposites. For instance, the electronics sector employs elastic, easily processable, and strong materials with high dielectric constants. The discovery of materials comprised of a single element with all the abovementioned characteristics is challenging.

In recent years, there has been enormous curiosity about polymer nanocomposites. There are diverse kinds of nanoparticles, which are available in the market and may be amalgamated into the polymer matrix for the production of polymer nanocomposites. Polymer nanocomposites contain a polymeric material, such as thermosets, thermoplastics, or elastomers, including strengthening nanoparticles. It is possible to integrate polymer as the polymeric species itself or by using the

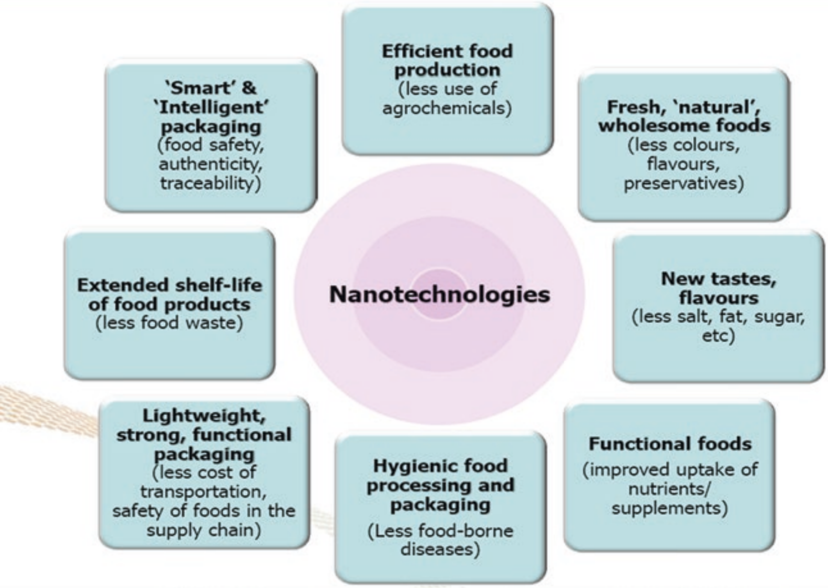
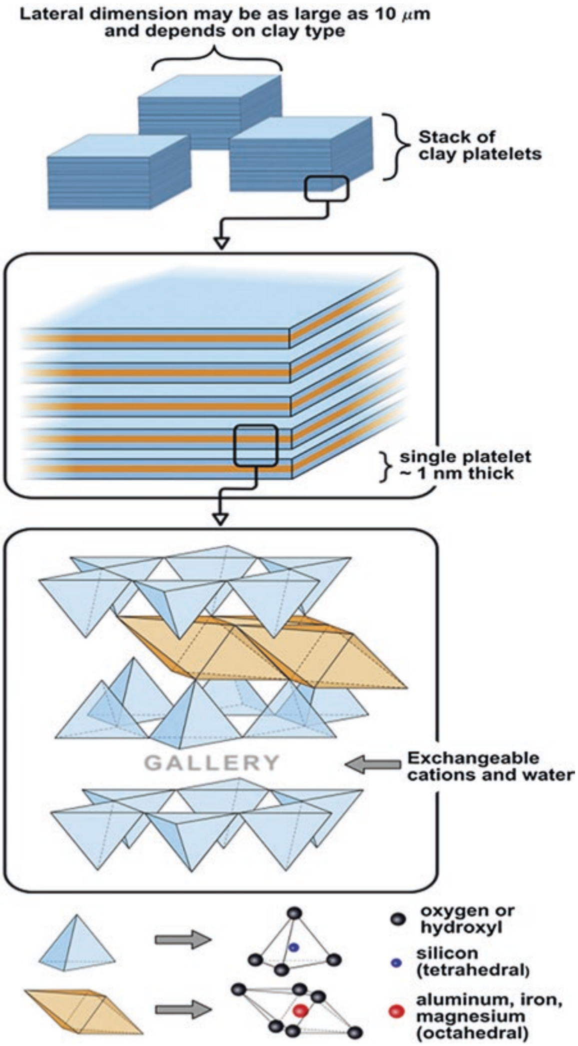


Fig. 6.3 Distinctive properties for many advanced applications

monomer polymerized in situ for providing the relevant polymer clay nanocomposite (Sarier et al. 2010; Duncan 2011). Nanoparticles that are used at most include montmorillonite organoclays (Fig. 6.4); polyhedral oligomeric silsesquioxane; carbon nanofibers; carbon nanotubes, with a small diameter and single wall; nanosilica (N-silica); nano-titanium oxide (TiO_2); and nano-aluminum oxide (Al_2O_3). Furthermore, an important role in defining the mechanical features of nanocomposites belongs to the quantity of nanoparticulate/fibrous, which is added to the polymer matrix. Their addition is mostly performed in minute amounts, which causes enhanced characteristics. Thermoplastics and thermosets utilized as matrices in order to produce nanocomposites comprise (Song et al. 2009) of montmorillonite organoclays (Fig. 6.4) and polyolefin, such as polypropylene, polystyrene, polyurethanes, polyimides, and ethylene vinyl acetate (EVA) copolymer.

The characteristics of materials may differ at the nanoscale due to two primary causes. Firstly, there is a comparatively larger surface area of nanomaterials in comparison with the identical mass of materials manufactured in a greater size. Secondly, quantum effects can commence to dictate the matter behavior at the nanoscale. Nanocomposites are the blends of nanomaterial fillers such as clay or fibers (including cellulose and silica) with polymers, which are combined into or coated onto the packaging. The filler materials generate a "tortuous path" for gases, making it difficult for water vapor and oxygen to diffuse through the package wall. It is also assumed that the nanoparticulate filler affects the barrier by varying the polymer matrix. The most commonly used nanoscale fillers include clays with typical levels of 1–5% added. The clay platelets are considered as highly dispersed or

Fig. 6.4 Structure of montmorillonite – phyllosilicate clay (Duncan 2011)



"exfoliated" structures with a high surface area to volume rate. There are several corporations that propose nanoclay formulations that can be employed in multilayer applications for plastic packages and films to look after oxygen-sensitive beverages and foods. Paperboard can also be coated with nanocomposite that has the added benefit of providing extra strength and firmness as well as an improved barrier.

For the purpose of acquiring the enhancements in polymer composites, a tiny amount of clay may be incorporated into the polymer matrix. The process in question is termed solid layer dispersion in polymers, and it includes two main phases, being intercalation and exfoliation presented in Fig. 6.5. The release of the clay particles from the system in question and their dispersion in the matrix polymer without the evident interactions between particles take place during exfoliation. The

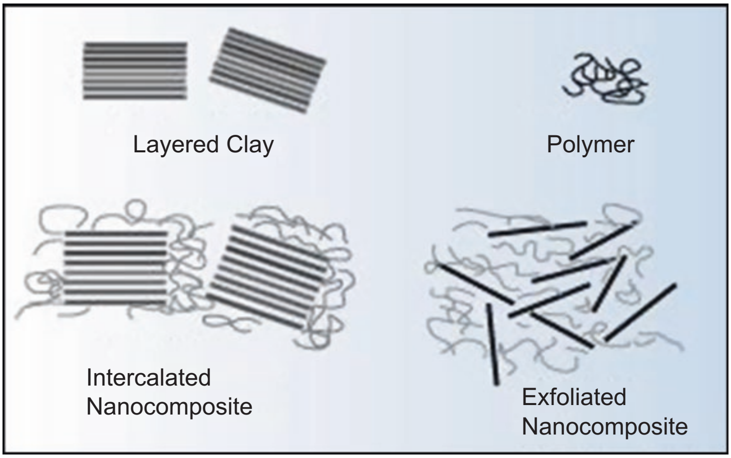


Fig. 6.5 Clay dispersion (Sorrentino et al. 2007; Rzayev et al. 2012)

layers of nanoclay interlaced into the structural matrix of polymers represent its outcome. It has been revealed that the general mechanical strength and barrier features of the material are considerably expanded by introducing the dispersed clay layers into the polymer matrix structure, and therefore, the usage of nanocomposite films becomes technologically possible (Sorrentino et al. 2007; Garcia et al. 2010). The dispersion of a filler material into nanoparticles making flat platelets ensures the building of polymer nanocomposites. Afterwards, the dispersion of the above-mentioned platelets into a polymer matrix occurs, which generates many parallel layers causing the passage of gases through the polymer in a torturous path, making complex (Rzayev et al. 2012).

In this chapter, the investigations and the anticipations on the implementations of nanotechnologies in the packaging industry and their applications are mentioned. Furthermore, very imperative information on the food-grade nanoparticles, their manufacturing and characterization, and security of food products manufactured by nanotechnology is covered. Biopolymer-based nanocomposites are also presently under development to integrate nanoscale supplements for regulated or increased compostability in plastics. Sensor and indicator technology for food safety and quality is a new research area (e.g., noninvasive gas detection or microbiological detection methods). Against counterfeiting, security inks or nanobarcodes can be employed. Another area of development is for edible coating applications on perishable foods to provide a moisture barrier, gas exchange, and delivery of antioxidants and enzymes, colorings, and flavors.

6.3 Applications in Food Packaging

Although there is an enormous potential for nanotechnology applications in food packaging, they have not become ordinary. The industry has been delayed mostly due to consumer wariness, as well as environmental and regulatory fears and high costs due to development and manufacturing.

The cases of the significant connections of nanotechnology to the engineering and science of agriculture and food systems include food safety, disease treatment delivery methods, novel mechanisms for cellular and molecular biology, innovative materials for the determination of pathogens, and environmental protection (Fig. 6.3). The following are considered to be the illustrations of nanotechnology as a means of ensuring advanced developments in the food sector (Petersen et al. 1999; Wesley et al. 2014):

- Improved safety of production, processing, and transportation of foods by means of sensors for the determination of pathogens and contaminants
- Instruments to uphold historic environmental records of a specific product and monitoring of individual transportations
- Systems which deliver the incorporation of sensing, localization, informing, and remote control of foods (smart and intelligent systems) and which are capable of improving the efficiency and safety of the processing and conveyance of food products
- Carrying, protection, and delivery of functional food constituents to their particular place of activity provided by encapsulation and delivery systems

Metal, ceramic (glass), and paper (cardboard) are the traditional materials for food packaging. Although these materials are still in use, plastic is becoming an appealing option for food packaging essentially due to the small weight, being inexpensive, simplicity for processing and formability, and outstanding variety of physical features of organic polymeric materials (Fig. 6.6). Polyolefins including polypropylene (PP) and different grades of polyethylene (HDPE, LDPE, etc.), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) represent polymers most often utilized for the packaging of food products. However, they are not limited to the abovementioned materials. Despite the radical changes brought by polymers to the food sector and their abundant benefits when compared to orthodox materials, their characteristic permeation to gases and other molecules of a small size constitutes their main disadvantage (Song et al. 2009; Duncan 2011).

Figure 6.6 (a) shows the newly wrapped package with both indicators of blue color, (b) represents the indicators right after their having been activated by UVA light, figure (c) demonstrates that the color of the indicator placed outside the package changes to blue following several minutes of exposure, while the color of the indicator in an atmosphere without oxygen stays white, (d) until the opening of the package, when the oxygen inflow changes the color again to blue. The system in question can be utilized for the easy and noninvasive determination of the existence of outflows in all packages instantly after manufacturing and at markets.

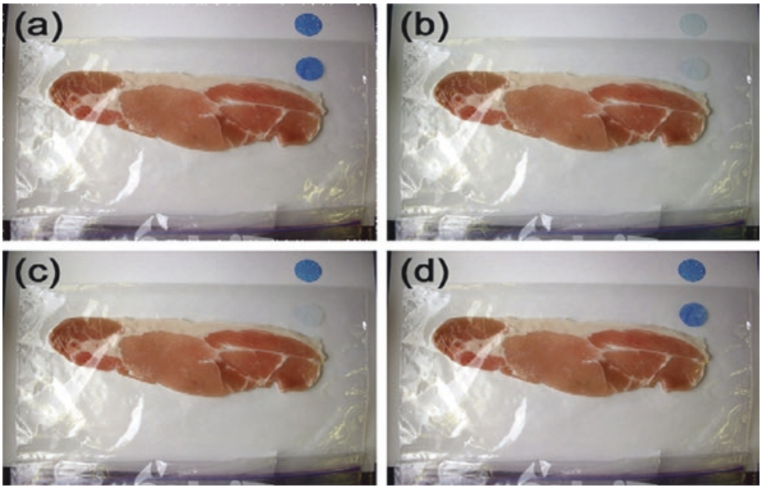


Fig. 6.6 Photographs of O_2 sensors using UV-activated TiO_2 nanoparticles and methylene blue indicator dye, one of which is put inside of a food package flushed with CO_2 and one is put outside (Duncan 2011)

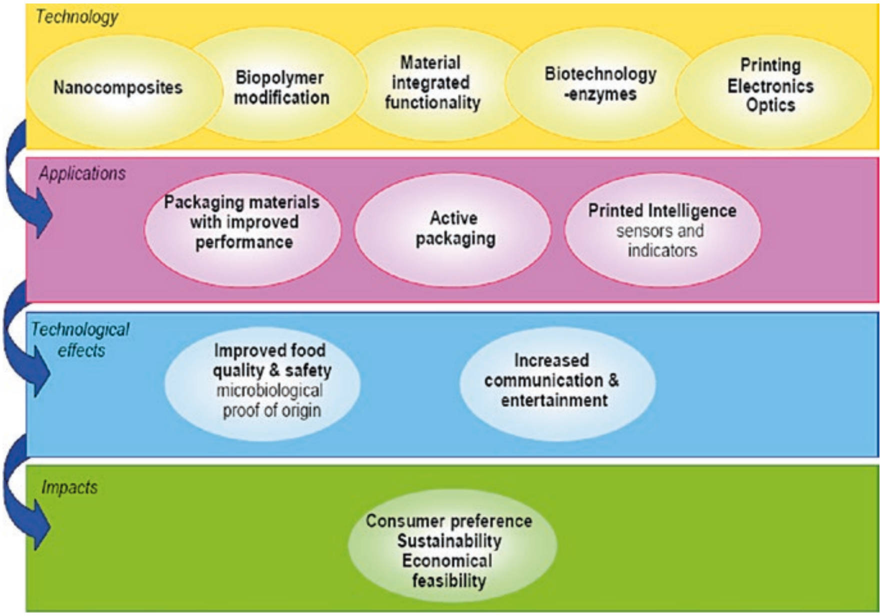


Fig. 6.7 Potential of nanotechnology in packaging

The usage of the biodegradable and edible film has increased as a result of the implementation of nanotechnologies, which has been associated with enhancements in the general functionality of biopolymers, improving their thermal, mechanical, and barrier characteristics, generally only at extremely low levels (Fig. 6.7).

Consequently, nanoparticles have a significant role in expanding the usage of biopolymers diminishing the leftovers of packaging that accompany processed foods and supporting the conservation of foods through prolonging their shelf life.

Information on product features and the circumstances of their storing and transportation commands the vital barrier characteristics of the materials employed for packaging in certain practices. The barrier characteristics comprise the permeation of gases, such as CO_2, O_2, N_2, ethylene, etc., water vapor, light, and aromas. The abovementioned characteristics constitute the essential factors for upholding food quality. Nevertheless, the selection of materials used for packaging cannot be limited only to their barrier characteristics. The factors, such as mechanical characteristics, for example, elongation, tensile and tear strength, burst strength, resistance to punctures, friction, etc., process ability, migration and absorption (general and specific), and resistance to chemical substances, should also be considered. The actual interaction of the food in packages with the material used for packaging makes the situation more complex since the original mechanical and barrier characteristics of the materials used for packaging can be modified as a result of this (Petersen et al. 1999). The uses of food contact materials employing nanotechnology are listed below:

- Food contact materials to increase packaging properties (i.e., gas barrier characteristics, flexibility, temperature and moisture stability, transparency, resistance to light and flame, and mechanical stability).
- Nanoclay-based composite-based packaging materials.
- Bionanomaterials in packaging applications.
- Biodegradable polymer nanomaterial composites which are produced as a result of adding inorganic particles, for example, clay, into the biopolymeric matrix, and the control of which can be performed with surfactants utilized for the layered silicate modification.

6.3.1 Enhanced Packaging

Adding of nanomaterials into the polymer matrix is performed for the purpose of expanding the gas barrier characteristics, in addition to humidity and temperature resistance of the packaging. Including of nanomaterials along with embedding nanocrystals and nanoclays enhances the barrier characteristics of the materials used for the packaging of dairy and food products. The benefit of clay nanocomposite in the material used for packaging brings up the increased shelf life, shatterproofness, small weight, and heat resistance (Brody 2003, 2007). However, the usage of both natural and synthetic biopolymers has been caused by the growing need for the manufacturing of biodegradable packaging. Chitosan, cellulose, and carrageenan represent the examples of natural biopolymers, whereas polyvinyl alcohol, polyglycolic acid (PGA), and polylactide (PLA) represent the examples of synthetic biopolymers (Rhim et al. 2013). Within the fillers utilized at the nanoscale, montmorillonite is frequently utilized because of a number of the benefits it provides, for example, its being inexpensive (Silvestre et al. 2011).

6.3.2 Active Packaging

Higher protection properties of the product are ensured as a result of the usage of nanomaterials interacting directly with food products and surroundings. For instance, antimicrobial characteristics may be delivered by silver coatings and silver nanoparticles, along with the use of other materials, for example, UV and oxygen. Furthermore, it is anticipated that nano-silver, nano-magnesium oxide, nano-titanium dioxide, nano-copper oxide, and carbon nanotubes will be utilized in food packaging with antimicrobial properties in the future. It is considered possible to cease microbial development when the customer opens the package and rewraps it using an active film part of the package by the implementation of active packaging (Morillon et al. 2002; Sandhya et al. 2010). The stated ways of the antimicrobial influence of silver nanoparticles are as follows: toxicity silver ions set free from inside of the nanoparticles produce, cellular destruction by silver atoms unconstrained from the nanoparticle surface, and the destruction of the cellular membrane structure by bound nanoparticles (Duncan 2011; Ramachandraiah et al. 2015).

6.3.3 Smart/Intelligent Packaging

Smart/intelligent packaging is aimed at detecting microbial and biochemical alterations occurring in the food, such as perceiving certain pathogens that develop in food products, as well as particular gases emerging from food deterioration. Moreover, certain "smart" packaging has been industrialized for the purpose of being utilized as a means of tracking of food security or avoiding fake products. Nanobiosensors are used to show the quality of foodstuffs and nanobioswitches are used to release preservatives (Scrinis and Lyons 2007). Furthermore, the genuineness of the food is certified by smart packaging. Therefore, protection against fake products is ensured. Additionally, the initial objective of creating smart packaging was to control the food package integrity. The history of time temperature and the date of expiration can also be monitored with the addition of gadgets. It is possible to determine toxins, microbes, and chemicals with the gadgets, for example, nanosensors, included in the packaging (Silvestre et al. 2011). There is a number of inventions in smart packaging, for example, oxygen scavengers and agents that control moisture; and packaging instruments regulating volatile flavors and smells, including flavor and odor absorbers; and leading-edge progresses in food packaging dissemination, for example, determination of radio frequency and electronic product codes. The purpose of intelligent/smart packaging is controlling and providing data on the quality of food products (Brody 2003). When the technique of radio frequency identification becomes more conventional in the food sector, it will become essential to integrate the food science knowledge for advancing the implementation of intelligent food packaging for the quality and security of food.

6.3.4 Nanocoatings

Nanocoatings are for antimicrobial and self-cleaning food contact surfaces. Waxy coating is employed extensively for certain foods like cheeses and apples. Lately, it has become possible with nanotechnology to develop edible coatings at the nanoscale up to 5 nm in width that the human eye cannot perceive. At present, edible films and coatings are utilized in numerous foods, such as vegetables and fruits, meats, chocolate, cheese, candies, products of bakery, and French fries. The abovementioned films and coatings can function as barriers against moisture, lipids, and gases (Kuzma 2010). Nevertheless, it is noteworthy that the properties of the nanomaterials employed in layers determine the characteristics of the edible coatings in question (Weiss et al. 2006). At present, polysaccharides, proteins, and lipids are utilized in layers. It is possible to perceive various abilities based on the kind of biopolymeric nanoparticles involved in the coating. Lipid-based layers function as moisture barriers. However, they do not have an effect on preventing gases, and they have insufficient mechanical strength.

Nanotechnology is fast evolving from the research laboratories onto the shelves in supermarkets and tables in our kitchen, and the transformation of food systems is possible with nanotechnology (Scrinis and Lyons 2007). Moreover, global commercial foods and food supplements comprising incorporated nanoparticles become accessible. Great advantages for food quality, security, and shelf life are assured by nanotechnology, which may overcome the difficulties it causes. The usage of nanotechnology in different applications for packaging systems and security is addressed in the present study from a critical aspect (Hills 2008).

6.4 Conclusions

1. As can be seen from all the research conducted, remarkable benefits for pioneering advancements in food packaging, from which customers, as well as producers, can benefit, are evidently ensured by nanotechnology. The implementation of nanotechnology demonstrates substantial benefits in enhancing the characteristics of the materials used for packaging. However, we are still in the beginning and, sustained investments will be necessary for financing studies and development for a deeper understanding of the benefits and shortcomings of the nanotechnology usage in materials utilized for packaging.
2. Nanotechnology is transforming the materials' world. Its influence on creating the next era of composites having the improved performance and numerous implementations is extremely high. The information about processing, description, and implementations provides scientists with benefits for comprehending and utilization of the specific material and chemical principles which determine the abovementioned innovative polymer nanocomposites. Despite nanocomposites' enabling various major implementations in different areas of the industry, some main technical and economic obstacles hinder their extensive commercialization.

3. The usage of nanoparticles for manufacturing the plastic packaging that alters its color when food is spoilt represents one of the remarkable developments. Physical and chemical mechanisms represent two major ways to undertake the abovementioned. A chemical indicator altering its color when the gases released during the oxidation of food are present is employed in the chemical one. Nanoparticles added into the polymer layers and modifying their optical characteristics according to their approximate position in the lattice structure are employed in the physical mechanism. It is possible to design this in such a way that a strong color is formed in the case of stretching the packaging, generating an evident sign of the decomposition that releases gases.
4. Forthcoming tendencies comprise the expansion of the nanotechnology in question to other kinds of polymer systems, in which the extension of novel compatibility approaches will probably become a requirement. Nevertheless, the manufacturing of PVC-based systems is still far away, and some difficulties in PET nanocomposites still need to be resolved. At present, studies are conducted on the further strengthening of clay nanocomposites by using glass fiber. Moreover, developing clay nanocomposites that conduct electricity is also interested in. Whereas studies are being conducted on the abovementioned aspects at present, significant and interesting advancements in nanotechnology for packaging will undoubtedly occur in the upcoming years, which can be presented as an example for developments in all commercial implementations of nanotechnology.
5. Nanotechnology which brings up many advantages varying from a better quality of food products and security to decreased agricultural inputs and enhanced processing and nutrition can pose threats for the usage and consumption by people and the environment. Further studies at the national and international levels are needed to provide the safety of technology and the highest food security and individual health protection. Protein and carbohydrate-lipid-based nanostructures can deliver preferred properties to food products in the form of content and flavor. Along with the applications of the nanotechnological developments in agriculture and food sector, unsafe nanomaterials and guidelines that are related to toxicity should carefully be taken into consideration. The advent of nanotechnological developments and the introduction of the usage of nanodevices/nanomaterials prompted new applications in agriculture and food sector. It was initiated to design packaging materials for the resolution of some problems that have been come across in these sectors. In case the techniques of radiation curing are associated with nanostructured polymers, it is possible to acquire strong and extremely tough films. While substantial fundamental study activities are presently ongoing in some European countries and Indian academic institutions, as well as national research laboratories, instant studies on the development-cum-presentation of products must be considered in the active cooperation with the industrial sectors in the country.
6. Furthermore, how regulatory agencies hold the developing technology in question determines the prospects of nanofoods. The massive possible advantages presented by nanotechnology should be balanced against the possible threats of

the usage and wrong use of nanomaterials, and most of the abovementioned threats are being assessed at present. Considering food products and materials used for food packaging including materials at the nanoscale, it is still required to fill in numerous gaps in data for exhibiting product security to worried people. As a consequence of the abovementioned examinations, how the public accepts foods including or using nanomaterials will depend mostly on how much people trust businesses and the government in shielding them from unidentified threats.

7. Nearly, each aspect of the food industry will be somehow affected by nanotechnology. The present chapter has debated to some extent several most encouraging implementations, such as materials used for food packaging with tremendously high barriers against gases and antimicrobial characteristics and nanosensors capable of sensing microorganisms as well as chemical pollutants in astonishingly low quantities. Nanoencapsulants for the purpose of the delivery of nutrients, tastes, and smells, more effective pesticides, security inks and nanobarcodes aimed at protecting against counterfeiting or holding the identity of products, and nanoparticles that may be employed in the intended genetic engineering of cattle and plant organisms related to agriculture constitute other possible spheres of the use of nanotechnology in the food sector that have not been addressed here.
8. It is possible to make food products more delicious, more useful for human health, and richer in nutrients, to produce novel food products, innovative packaging, and storage technologies of food products with nanotechnology. Nevertheless, most of the implementations are presently at a simple stage, and they target products with the high nutritional value, at least in the short period of time. Besides, it is possible to use nanomaterials in order to produce packaging, inside which the product remains fresh for a longer period of time. Data on the condition of food products can also be delivered by smart food packaging with integrated nanosensors. There are nanoparticles in food packages, which inform customers about the safety of a food product. Sensors may alert before the food is spoilt or notify of the ingredients in the content of food products precisely. Indeed, the packaging business, in general, will be redefined by nanotechnology.
9. A number of thrilling advantages presented by nanomaterials to the food sector that comprise improved materials used for food packaging, in addition to reliable foods in supermarkets, with the lower chemical contamination and containing less possibly life intimidating microorganisms have been demonstrated in this chapter. The implementations examined in this chapter were explicitly selected since they are the most probable nanofood products, which will be recognized by customers in a short period of time. Nonetheless, food nanotechnology is developing, and the prospects of the stimulating research area in question are mainly indeterminate at present.

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Nanobiosensors, as a Next-Generation Diagnostic Device for Quality & Safety of Food and Dairy Product

7

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Abstract

Nanotechnology and biotechnology are a sole combination and generate a new advanced discipline: nanobiotechnology. It includes the application of the tools and processes of nanotechnology to study and manipulate biological systems. Nanobiosensor is an advanced, analytical technique designed and developed by nanotechnology and biotechnological applications. They have remarkable benefits with cost-effective, high selectivity, specificity, more rapid, robust, and sensitive quantitative techniques for field analysis capability. These techniques have proved to be the best tools to ensure food and dairy product quality and safety. This chapter focuses on the potential role of nanomaterials (gold, magnetic, carbon nanotube, silver nanoparticles, etc.), which are currently being used in various nanobiosensors to find various chemical adulterants, different toxins, and harmful pathogens. Analysis of food and dairy products for adulterants, such as starch, urea, hydrogen peroxide, neutralizer, detergents, boric acid, melamine, mycotoxins, and bacteria, is performed. Various nanobiosensor used for this purpose are nanowire biosensors, ion channel biosensor, cantilever biosensor, and optical biosensor.

Keywords

Nanobiosensor • Adulterants • Diagnostic device

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7.1 Introduction

Nanotechnology is a new developed discipline that has scientific equipment and modified material that involves changes in chemical and physical properties of any matter at molecular or nano levels. Alternatively, the technique and knowledge of basic biology are used by biotechnologists to change at the level of genetic, molecular, or nano and cellular processes for the development of products and services. Its use ranges in areas from medicine to the agriculture field. Nanotechnology and biotechnology are the sole combination and generate a new advanced discipline: nanobiotechnology. Nanobiotechnology is biotechnology at the nanoscale. It includes the application of the tools and processes of nanotechnology to study and manipulate biological systems (Fakruddin et al. 2012). By using this technique, nano or molecular level instruments can be formed by simulating or using the technique of basic biology to make tools to control and study different properties of living systems at the molecular level. Nanobiotechnology is an innovative science and easier for the life science or many field current issues. This technology has the capability to design and give a shape of our recent concept and simplify the understanding by removing borders between biology, physics, and chemistry. Therefore, new challenging concepts and directions give us better facilities in the field of diagnostics and other disciplines limited by the extensive use of nanobiotechnology with the passage of time.

7.2 Nanotechnology: Impact on Food and Dairy Product Quality and Safety

Recently, there has been increased awareness of consumers for food and dairy product safety and quality. An important requirement is to provide a high-quality and safe dairy product. Mainly conventional methods are used to check quality of food and dairy products, and it is high sensitivity and accuracy but is expensive and requires trained manpower. Analysis requires a rapid, reliable, and cost-effective method.

To ensure food and dairy product quality and safety, analysis of such food and dairy products for adulterant, such as starch, urea, hydrogen peroxide, neutralizer, detergents, boric acid, melamine, and mycotoxins, is very important. Comparison with presence of adulterants is important to follow the minimum limits set by governmental food authorities worldwide. Most analysis tests of these adulterants are analyzed by conventional methods (Vidal et al. 2013). However, new techniques have been develop to analyze these adulterants, i.e., nanobiosensor technique, which is a quick, reliable, sensitive, and cost-effective measureable method for the field level testing ability. By applying these techniques, the nanomaterials used in sensor, i.e., nanobiosensor development is more benefiting in adulterant analysis and developing ultrasensitive devices with nanobiotechnology and its impact.

Recent developments performed in the field of nanotechnology and bionanotechnology permit the design of an innovative class of analytical systems: nanobiosensors. The major advantages of nanobiosensors include affordability, high degree of automation, highly specific, and selective. Due to these characteristics, an increase in the number of devices has been described in the field of food and dairy product for the diagnosis purpose. The medical sector played a crucial and protuberant role in the development of many novel technologies. Many research efforts were performed for the development of biosensors to check the blood glucose level in a diabetic patient. Later, this application of biosensor was used in new ways in other field applications, such as food, dairy product, and environmental control.

7.3 Understanding Sensor, Biosensor, and Nanobiosensor

In developing countries, the availability of medical diagnostic laboratory is very limited. There is requirement to develop instruments or devices that are convenient, accurate, and inexpensive for the fast analysis or diagnosis of human disease, environmental monitoring, and for food and dairy product safety. Recently, the importance of nanobiosensor and other technology has increased using nanobiotechnology to expose agricultural adulterant.

A *sensor* is a device that is able to identify and respond to input, e.g., light, heat, motion, moisture, pressure, or any other from the physical environment. The signal is an output that is converted to a readable display at the sensor location or transmitted electronically over a network for reading or further processing (Arnold and Meyerhoff 1988). *Biosensor* is "an analytical device that includes a biologically active substance with proper physical transducer to produce a computable signal, which is proportional to the concentration of chemical species in any type of sample" (Belkin 2003; Eggins 2002; Wilson and Gifford 2005; Wilson 2005; Dorothee et al. 2008). *Nanobiosensor* is able to detect any biophysical and biochemical signal associated with a particular analyte (molecule). This presented nanobiosensor can be merged into other technologies, such as lab-on-chip, to facilitate molecular diagnostics or microfluidics device for the analysis of food and dairy product adulterant (Yachna et al. 2009).

7.3.1 Basic Principles of a Biosensor

Biosensor development is the multidisciplinary research field. It requires the involvement of various fields, such as biochemistry, biology, microelectronics, physics at the micro and nanoscale, and surface chemistry. In general, a sensor is defined as a device that can produce an electronic signal resulting in external stimulation and allow the quantification of several physical (pressure, temperature, and mass) or chemical (pH and O_2) properties. Biosensors are biological components, such as protein, enzymes, oligonucleotide, cells, and tissue, included and used to generate particular signal towards the objective component.

A schematic representation of the working principle of a biosensor is shown in Fig. 7.1. Specific biosensor is considered by three main aspects: 1) biological

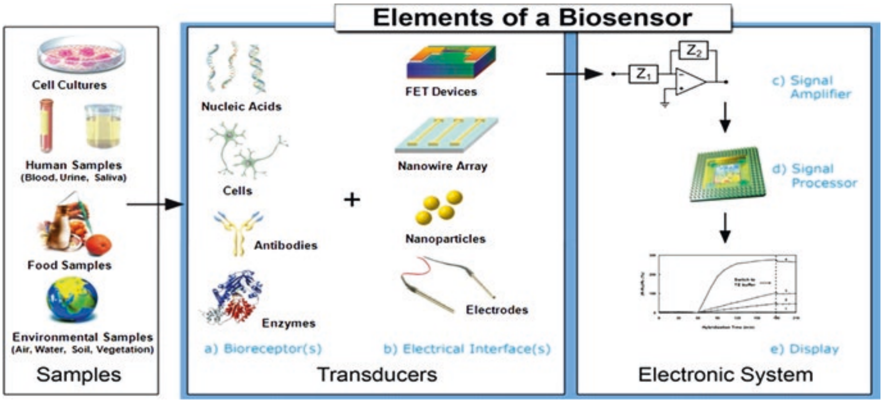

Fig. 7.1 Elements of biosensor includes sample, transducers, and electronic system

recognition element; 2) transducer system; and 3) recognition element with the transducer system (Arnold and Meyerhoff 1988). Examples of nanobiosensors follow.

7.3.1.1 Nanowire Biosensors

One of the nanobiosensors class is nanowire biosensors. The nanowire is made of sensing components, and it is covered by biomolecules, such as deoxyribonucleic acid (DNA), proteins, polypeptides, filamentous bacteriophages, and fibrin.

7.3.1.2 Ion-Channel-Based Sensing

All living cells membrane is formed by protein molecules, and the biological ion channels are hydrophilic sub-nano-sized pores from which biological ion channel fused is formed by protein molecules. Regulation and control of electrical and biochemical activity inside and outside of the cell are monitor through this channel. The development of new generation's nanobisensors control of molecular ion channels is switched by the recognition event.

7.3.1.3 Cantilever Biosensors

Using the flexibility characteristics of cantilever technique can analyze various biomolecules, such as DNA, proteins, vapors, ions, antibiotics, and pathogenic microbes by chemical/biological sensor. The changes in surface of molecules is recognized by static mode techniques, which is more sensitive to molecular interactions, i.e., change in the electronic charge distribution of the substrate's surface atoms and by lateral interactions within the next molecular layer: structural changes and electrostatic forces.

7.3.1.4 Optical Nanosensors

Optical nanosensors are commonly used for the detection of pathogen based on fluorescence and surface plasmon resonance (SPR). This technique is generally based on monitoring the change in the optical signal, which occurs between the functionalized pathogen and nanomaterial. The greatest advantage of this technique is that the sensor can incorporate into the deeper part of cell with negligible disturbance of cell. Nanomaterials, such as gold, magnet, and quantum dots, have strong optical properties that can provide excellent optical labels to improve the sensitivity of optical transducer surface of nanosensor. Optical transducers are mostly attractive for developing the strong device that is easy to use, portable, and cost-effective.

7.4 Nanoparticles in Nanobiosensor

To improve the performance of the existing devices for potential sensing, researchers tend to incorporate nanoparticles used for biosensor construction. Recently, variety of nanoparticles with their *specific* properties, such as small size, high speeds, *lesser* distances for electrons to travel, lower power, and lower voltages. Different types of nanomaterials are utilized, such as super-paramagnetic nanoparticles, bucky balls and carbon tubes, liposomes, nanoshells, dendrimers, quantum dots, and nanorods, to increase the electrochemical signals of biological interaction events that occur at the electrode/electrolyte surface. Functional nanoparticles that attach to biological molecules, such as DNA, peptides, enzyme, and proteins, have been developed for use in nanobiosensors to detect and magnify various signals from biological material (Touhami 2011; Sagadevan and Periasamy 2014). Table 7.1 summarizes the role of various nanomaterials in the detection of contaminants, such as melamine and carbofuran with their minimum sensitivity.

7.4.1 Super-Paramagnetic Nanoparticles

Super paramagnetic nanoparticles bind to a magnetic field but do not hold in magnetism after the field is removed. For the magnetic bioseparation 5–100 nm size in diameter, iron oxide nanoparticles have been used. Many techniques have been used to coat the iron oxide nanoparticles with gold, silica, antibodies of cell-specific antigens, and for separation from the medium. It also is used for drug delivery and gene transfection in membrane transport studies. External magnetic field can accelerate the magnetic nanoparticles towards target tissue along with bioactive molecules or DNA vectors and drugs. It also is useful as magnetic resonance imaging contrast agents (Basa 2007).

7.4.2 Bucky Balls and Carbon Tubes

Bucky balls and carbon tubes are structural class of fullerene. Bucky balls are round in shape, whereas carbon tubes are tubular. The size of a carbon tube is several nanometers in diameter, but the length can be much larger. It can be several millimeters, depending on its use. Due to strength and unique electrical properties of carbon tubes, it has many applications in materials science, drugs, and for vaccines

Table 7.1 Various nanoparticles use to detect food and dairy product adulterants

Nanomaterials	Food and dairy product adulterants	Sensor/probe	Sensitivity	References
Gold nanoparticle	Melamine	Colorimetric probe	0.4 mg/L	Sonawane et al. (2014)
		Standard colorimetric card	1–120 mg/L	Li et al. (2010)
		Surface-enhanced Raman spectroscopy	100–200 μg/L	Zhou et al. (2011)
Water-soluble CdTe quantum dots	Melamine	Fluorescence probe	0.04 mg/L	Mecker et al. (2012)
Single wall carbon nanotube	Melamine	Electrochemical luminescence	1×10^{-13} M	Zhang (2012)
Gold nanoparticle and PB-MWCNTs-CTS	Carbofuren	Electrochemical immunosensor	0.1–1 μg/mL	Liu et al. (2011)
Carbon nanotubes (CNTs)	Food borne Bacterial Pathogens	Electrochemical sensor	1.6 × 104 CFU/mL	Sun et al. (2012)
Magnetic nanoparticles and TiO_2 nanocrystals	*Salmonella*	Optical nanocrystal probes	100 CFU/mL	Jain et al. (2012)
Oligonucleotide-functionalized Au	*Escherichia coli* O157:H7	Piezoelectric biosensor	1.2×10^2 CFU/mL	Joo (2012)
Gold nanoparticles	*Staphylococcal Enterotoxin B*	Chemiluminescence (ECL)	0.01 ng/mL	Chen et al. (2008)
Au NP–PAADs	Brevetoxins	Electrochemical immunosensor	0.03–8 ng/mL	Schofield et al. (2007)
Functionalized-gold nanoparticles	Aflatoxin	Immunoelectrode	10–100 ng dL^{-1}	Yang et al. (2008)
Silver core and gold shell (AgAu)	Aflatoxin B1	Immunodipstick assay	0.1 ng/mL	Tang et al. (2011)
Antigen-modified magnetic nanoparticles and antibody functionalized upconversion nanoparticles (UCNPs)	Aflatoxin B1 (AFB1) and ochratoxin A (OTA)	Immunosensing probes and signal probes	0.01 to 10 ng/mL	Sharma et al. (2010)

(continued)

Table 7.1 (continued)

Nanomaterials	Food and dairy product adulterants	Sensor/probe	Sensitivity	References
Nanostructured zinc oxide	Mycotoxin	Indium–tin–oxide (ITO) glass plate	0.006–0.01 nM/dm^3	Liao and Li (2010)
Single-walled carbon nanotubes (SWNTs)	Ochratoxin A (OTA)	Fluorescent aptasensor	25–200 nM	Wu et al. (2011)
Fe_3O_4 NPs	*Campylobacter jejuni*	Glassy carbon electrode	1.0×10^3 to 1.0×10^7 CFU/mL	Ansari et al. (2010)

as carriers. Carbon tubes have single and multiple wall structures and other types of tube forms, depending on size, shape, density, and other properties.

7.4.3 Liposomes

The most useful nanoparticle in pharmaceuticals and cosmetic industry is liposomes, because it is composed of lipid and because of its capacity for fusion inside the cells, once their delivery function has been occurred. The first originate nanoparticles used for drug delivery is liposomes, but it cannot release their loaded materials by fusing in aqueous environments and it managed by stabilization using substitute nanoparticles.

7.4.4 Nanoshells

The shape of nanoshells are spherical or round cores because of the specific compound coated into core, i.e., shell or outer coating layer and the thickness of shell is a few nanometers. Application of nanoshells is wide. It is used in biomedicine, pharmaceuticals, cosmetic industry, and diagnosis. The particular wavelengths absorbed by nanoshells depend on the thickness of the shell, which biologically useful. The construction of nanoshells by many materials, such as silica as a core and gold particles attach as a shell. We can replace silica particle with magnetic nanoparticles. Nanoshells such as these have been used to diagnose mycotoxins present in food and dairy products.

7.4.5 Quantum Dots

The only nanoparticles that emit all colours of the rainbow depending on size are quantum dots, also known as nanocrystals. They are semiconductors, nanometer-size particle. Quantum dots are applied in cancer imaging and cell labelling study. It restrains conduction of band electrons and valence band holes in all three special directions. Semiconductor nanocrystals and core-shell nanocrystals are examples of quantum dots.

7.4.6 Nanorods

Nanorods are mostly used in nanomedecines as imaging and contrast agent. The size of nanorods is usually 1–100 nm in length and made up of semiconducting materials, such as gold or inorganic phosphate, small cylinders of silicon, and other materials (Guo et al. 2011).

7.5 Various Methods Used for Synthesis of Nanoparticles

Nowadays, the researchers concentrate on the development of novel, simple, and sensitive techniques to formulate and stabilize nanoparticles. They also work on stable and monodispersed particles formation. By these methods, different metals, metal oxides, sulfides, polymers, core-shell, and composite nanoparticles can be prepared, which are mainly classified into two types: physical methods and chemical methods.

7.5.1 Chemical Methods

7.5.1.1 Chemical Precipitation

Conversion of soluble inorganic materials to soluble impurities was used for removing from the solution by some suitable reagents. It also is removed by flocculated and sedimentation. The removal of precipitate depends on the solubility of the product and is controlled by pH and temperature. Mainly this method is used in industrial wastewater treatment, and recently, researchers used this method for nanoparticle synthesis, such as iron oxide nanoparticles. The major advantage of the chemical precipitation method is that a huge amount of nanoparticles can be synthesized and the control of particle size distribution is limited, because only kinetic factors control the growth of the particles.

7.5.1.2 Vapor-Phase Synthesis

Nanoparticles formulation takes place in gas phase; therefore, this method is known as vapor-phase. In this synthesis technique, atoms and molecules are condensed in gas phase. It is not new; flame reactors are used to produce large quantities of nanoparticles by many multinational companies. Carbon black and titanium dioxide nanoparticles are synthesized by flame reactors.

7.5.1.3 Hydrothermal Synthesis

Hydrothermal synthesis can be defined as a synthesis technique of single crystal, depending upon the solubility of minerals in hot water under high temperature. The growth of the crystal is performed in a stainless steel pressure apparatus, called an autoclave, in which the nutrient media is supplied by dissolving in water. The temperature gradient is kept at the opposite edge of growth chamber so that the hotter end can easily dissolve nutrient media and the cooler end causes seed to take extra growth. The possible merits of hydrothermal technique compared with other typed of crystal growth method include the capacity to generate crystalline stage that is not stable at the melting point. Also in such material, higher vapour pressure near their melting point can be grown by this method. Hydrothermal technique is chiefly suitable for the growth of large good-quality crystal and it maintains good control over their composition.

7.5.1.4 Sonochemical Technique

In sonochemical technique, nanoparticles are synthesized by exposing the aqueous or organic distribution of precursor material using an ultrasonic probe at room temperature. The particle size achieve by this method mainly depends upon the concentration of solution and the time of sonication.

7.5.1.5 Microemulsion Technique

This is a newly innovative technique that can permit the preparation of ultrafine metal particles ranging from 5 to 50 nm in size. The degree of particle nucleation is the function of the filtration rate of micro emulsion droplets. In addition to short introduction on some aspect of microemulsion type and synthesis, we have mainly concentrated on the kinetics of metallic particle synthesis. The barrier of parameters, such as temperature, nature of metal salt, light, and reaction condition, also are studied. This result points out that the nature of stabilizer emulsifier, colloidal stability of microemulsion droplets, and surface activity of additives play crucial role in the particle size and dispersal during preparation of metal particles.

7.5.2 Physical Methods

7.5.2.1 Laser Ablation

In laser ablation, the matter from target surface evaporates with help of high-power laser pulses in such way that the stoichiometry of the material is preserved in the interaction. As a result, supersonic jet of particle (plum) is emitted ordinary to target surface. The plume, parallel to rocket exhaust, spread away from the target with fast forward-directed velocity sharing of the different particles. The condensation of evaporated species will occur on the substrate, which is positioned opposite to the target. The evaporation method occurred in vacuum chamber, either in the presence of some background gas or in vacuum. Oxygen will be the most common background gas in case of oxide films.

7.5.2.2 Sputtering

Sputtering technique is used to cover the thin film of specific material on to the surface of substrate. First, the gaseous plasma is created following acceleration of ions from the plasma into the target material. The target material is eroded by the incoming ions via energy transfer and then emitted in the form of neutral particles. It will be either single atom, bunch of atoms, or molecules. As the neutral particle will emitted, they will run away straight forward until they come in interaction with other particles or nearby surface.

7.5.2.3 Spray Rout Pyrolysis

Considerable size of particles are in nanometer (1–100 nm), which will be of more interest for different applications, extending from electronics via ceramics to catalyst. Due to their distinctive and enhanced property, it is primarily determined by its size, composition, and its structure. Quick, simple, and general method is used for the constant synthesis of nanoparticle with flexible sizes, narrow size distribution, high crystallinity, and better stoichiometry.

7.5.2.4 Inert Gas Condensation

The nanometer-sized particles are synthesized with help of inert gas condensation from metallic iron by evaporation and accumulation in flowing inert gas stream. Inert gas condensation is an expensive but also advanced technique in the field of nanotechnology. This technique is considered as a controlled method. By this technique, the exact shape and size of nanoparticles can be prepared. In this technique, nanoparticles quickly form collides with inert gas in low-pressure environment, and thus controlled and smaller nanoparticles are synthesized (Guo et al. 2011).

7.6 Applications of Nanobiosensor

7.6.1 Nanoparticle-Based Microfluidic Device for Detection of Food and Dairy Product Adulterant

Such a device may be invented using well-established and inexpensive manufacturing techniques, which make it suitable for the detection of adulterant in developing regions. Paper/thread is an alternative material that have the ability to combine with other hydrophilic/hydrophobic material to form contrast and liquid control for fabricating microfluidics system with nanoparticles. Several diagnostic methods can be used in combination with these materials, such as well-established colorimetric detection practice, immunoassay, and many others.

7.6.2 Detection of Allergens in Food and Dairy Products

A novel optical biosensor is developed by combining antibody or aptamer technology with the help of Plasmon Resonance technology, which is used for the detection

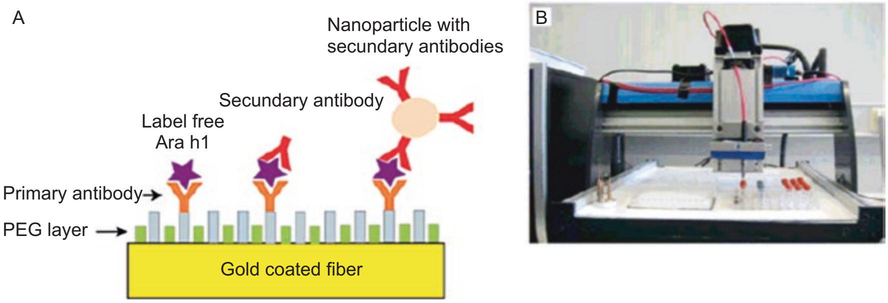

Fig. 7.2 (**a**) shows the working principle of the fiber optic SPR sensor. The bioreceptor molecules are immobilized on the nanoplasmonic sensor module, built around an optical silica fiber, coated with a thin (50 nm) gold layer. When allergens bind to the bioreceptors at the surface, the refraction index changes, which is monitored by an optical detector. Nanoparticles are used for signal enhancement. (**b**) Experimental set-up (Ai et al. 2009)

of allergens in food and dairy products. Biosensor has a couple of merits of optical fiber technology and the use of aptamer as a specific biorecognition element. This biosensor permits rapid, accurate, and label-free screening for the presence of food and dairy product allergens (Fig. 7.2).

7.6.3 Detection of Small Organic Molecules in the Food and Dairy Product

Nanosensors have the capacity to develop quick and accurate technique for industry, and regulatory agencies can detect the existence of food and dairy product adulterant or molecular contaminant in complex food and dairy products. These tests are based on observable color change, which occur to metal nanoparticles media in the presence of analyst, for example, gold nanoparticles (AuPNs) with cyanuric acid, which then selectively bind with melamine. The adulterant is artificially used to inflate the measured the protein content of foods and dairy products. The melamine encourage the accumulation that cause the gold nanoparticles to undergo a reproducible and analyte-dependent color change from red to blue. This can be used to measure accurately melamine concentration in raw milk and infant formula at concentrations as low as 2.5 ppb with naked eyes (Huang et al. 2010).

7.6.4 Detection of Microorganisms in Food and Dairy Products

The capacity to determine that food and dairy products are contaminated by virus, bacteria, or fungi will remain an important research objective. In real food and dairy product system, the most detection methods are needed for the isolation of organism from the nearby environment to confirm that signal-to-noise ratio are sufficiently large to observe. Immunomagnetic separation (IMS) is the technique used to fulfill

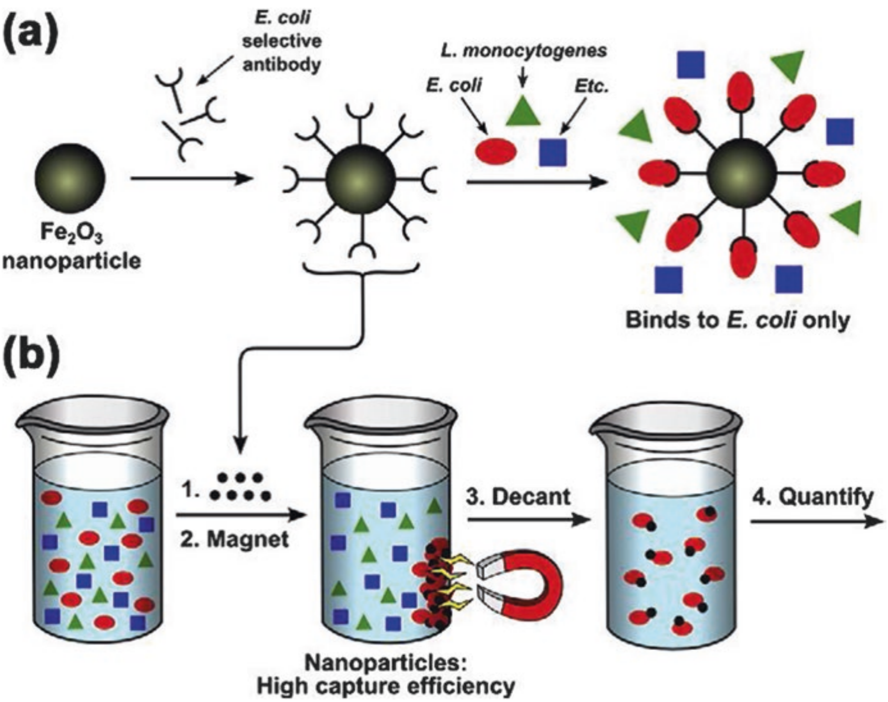

Fig. 7.3 Immune magnetic separation based on bacterial detection technique using magnetic nanoparticles (Ai et al. 2009)

this requirement. In this technique, magnetic particles bind with selective antibodies in mixture with magnet to isolate selectively the target analyte from the mixture of food and dairy product earlier to detection. Nanoscales magnetic particles are widely use in this concern because of their high surface-to-volume ratios, which can help to capture the large analyte efficiencies. Following capturing, the analytes can easily be purified and subjected to standard measurement technique. This technique is illustrated in Fig. 7.3 (Ai et al. 2009).

7.6.5 Detection of Gases in Food and Dairy Products

Oxygen content in food and dairy products is a primary factor that favours the growth of microorganisms. For the purpose of analysis the gaseous elements, the packages of the packed food and dairy products are not early destructed. In processing facilities, packaged food and dairy products are tested randomly during a production run, which is time-consuming, costly, and yet unreliable. A noninvasive method for continuous and easy monitoring of the gas content of a package headspace would provide a means to confirm the quality and safety of the contained food and dairy products long after it has left the production facility. On this view, nanosized TiO_2 or

SnO_2 particle-based photoactivated indicator ink for the detection of in-package oxygen level and redox active dye (methylene blue) has been developed. If a minute amount of oxygen is present, then detector will change colour. Although quantification of the oxygen content in food and dairy product packages might not be possible by this technology, it provides an easy and visual technique to detect modified atmosphere packages (MAPs) with possible compromised seal integrity.

A noninvasive technique for the determination of CO_2 content in MAPs is based on luminescent dyes, which are standardized by fluorophore-encapsulated polymer nanobead. The detecting range of CO_2 sensor is 0.8–100% with resolution of 1% and having 0.6% cross-reactivity with molecular oxygen. Detection of amine gas, which are the indicator of fish and meat spoilage, a hormone that leads to fruit ripening and for the detection of ethylene gas WO_3-SnO_2 nanocomposites, is applied. These all are examples of gas sensing associated with quality and safety of food and dairy products (Joyner and Dhinesh 2015).

7.6.6 Detection of Moisture in Food and Dairy Products

Nanoparticle-based nanosensors also have been developed to detect the presence of moisture content inside a food and dairy product package. Such a nanosensor for moisture detection is based on carbon-coated Cu nanoparticles dispersed in a tenside film. The inter-nanoparticle separation can occur by swelling polymer matrix in a humid environment. These changes in sensor strip can cause reflection or absorption of different color light, which is then easily monitored for rapid and perfect measurement of moisture level in packages without any invasive sampling (Duncan 2011).

7.7 Conclusion

Various nanomaterials integrated to develop various biosensors and nanbiosensors enable the use of biological components to bind and react with a target molecule and transduce generate detectable signals to help rapid detection of food and dairy product adulterants. They can play a crucial role in food and dairy product quality and safety and help to take rapid action when required. Thus, simple visual tests can be created and color changes can easily detected by even unskilled users, making it easier to test for harmful food and dairy product adulterants. From this chapter, it is clear that gold nanoparticles, magnetic nanoparticles, and carbon nanotubes can play a very important role for exposure of adulterants and toxins. Thus, nanobiosensor will be the next-generation diagnostic device for food and dairy product quality and safety. Further research work is required to explore such nanomaterials and new ones that could be used to improve food and dairy product quality and safety.

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Nano Molecular Imprinted Polymers (NanoMIPs) for Food Diagnostics and Sensor

8

Ibtisam E. Tothill and Mohammed J. Abdin

Abstract

The application of biosensors and diagnostics for food safety and quality continues to attract wide attention. Nevertheless, possible drawbacks of reliability, sensitivity and specificity in some complex foods matrices have limited their commercialisation in this field. With the developments in nanotechnology and the ability to synthesise novel nanomaterials with enhanced physical and chemical properties for diverse applications, their use in biosensor fabrication has revolutionised the technology and helped in overcoming some of these problems. The development of biomimics as nano molecular imprinting polymers (nanoMIPs) to replace antibodies as the sensing material in biosensors is overcoming problems of stability, sensitivity and cost associated with biomolecule-based sensors for specific applications. Nowadays nanoMIPs are being synthesised for a range of analytes detection including microorganisms and their toxins, environmental contaminants, pharmaceuticals and allergens. Many have shown potential application in the detection of these analytes in a range of matrices including food samples. In this chapter the design and synthesis of nanoMIPs and their use in the development of sensors and diagnostics and their application for foods sensing application will be reviewed and discussed.

Keywords

Nanomaterials • Molecular imprinted polymers • NanoMIPs • Biosensors • Food sensing

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8.1 Introduction

A wide range of nanomaterials have been developed in recent years for applications in biosensors and diagnostic devices with molecular imprinting polymers (MIPs) as one of these examples. Emerging challenges associated with food production and maintaining food diversity, safety and quality in the food chain have fuelled the need for novel detection methods that are rapid, accurate and sensitive for on-site analysis. This proactive approach requires a multidisciplinary system and advanced technologies in order to protect human health, reduce waste and control production costs. Hence, the need to analyse and monitor the different critical steps in the food chain, from raw materials, during processing, final products and during storage. There is also a need to control cross-contamination between different products for allergens and authenticity testing. The use of an integrated intelligence approach which will allow full interconnection and communication of multisensing systems also has advantages for food tractability. Therefore, a nanotechnology-inspired systems will be powerful in delivering and fulfilling these requirements (Tothill 2010a, 2011).

The interest in biosensor technology and rapid diagnostics devices in areas such as veterinary care, animal husbandry, food and process control and environmental analysis continues to expand. This has been due to the wide advantages these devices are able to provide, including rapid testing, cost-effective, specific and reliable quantitative and qualitative analysis. Therefore, emerging sensors based on micro- and nanosystems have emerged as an attractive option for food testing especially in cases where rapid analysis is required before food products reach the supermarket shelfs. While work in this field initially concentrated on the use of biological receptors as enzymes, whole cells and antibodies, much of the current research is focused on replacing these with novel synthetic nanorecognition materials to overcome some of the disadvantages of using biomaterials as sensing materials. Also this is a consideration where application of biomaterials are not suitable due to their poor stability, lack of performance or difficult to produce towards specific target analyte or expensive. These developments are also being combined with advances in transducer technology and emerging devices for multiplex analysis and nanotracking or mobile technology in the food chain. Awareness in nanomaterials emerged from the properties these materials exhibit when reduced to the nanometre scale compared to the bulk materials. The use of nanomaterials and structures such as semiconductors and conducting polymer nanowires and nanoparticles (carbon nanotubes, silica nanoparticles, dendrimers, noble metals nanoparticles, gold nanoshells, superparamagnetic nanoparticles, quantum dots, polymeric nanoparticles) for biosensor applications is expanding rapidly (Willner et al. 2007; Kerman et al. 2008). Examples of emerging affinity recognition materials include peptides (Heurich et al. 2013; Tothill 2010b), aptamers (nucleic acids based) (Zhao et al. 2012; Eksin et al. 2015: Chen and Yang 2015; Tzouvadaki et al. 2016) and nano molecular imprinting polymers (nanoMIPs) (Altintas et al. 2015a, b; Poma et al. 2013).

Methods used for the synthesis of MIPs are diverse, and recent development in producing them as nanomaterials has increased their specificity towards their target analyte and reduced the nonspecific binding associated with real samples analysis. This enhancement in their performance gained them great attention in recent years and increased their use as binding receptors in sensors (Abdin et al. 2015; Altintas et al. 2015c). However, the challenge is to produce MIPs that can compete with the natural molecules with respect to performance in environmental samples. This chapter is focused on the developments and advances taking places in the production and use of molecular imprinted polymers as nanoparticles for sensing application with focus on food and agricultural sensing.

8.2 Molecularly Imprinted Polymers (MIPs)

Molecularly imprinted polymers (MIPs) are synthetic polymeric receptor materials which can recognise and specifically bind to target molecules. MIPs are created by forming a complex between the template target molecule (an analyte of interest) and functional monomer(s) using either covalent or non-covalent bonds (Fig. 8.1).

MIPs prepared via non-covalent imprinting can interact with their target in a reversible way via a variety of interactions such as hydrophobic, electrostatic and ionic. A cross-linking agent is used in a polymerisation reaction followed by the removal of the template from the polymer which creates the specific binding sites. The produced binding sites are complementary to the template (analyte) in shape, size and orientation of the functional groups. MIPs follow the underlying principle of molecular recognition found in antibodies with antigens, hormones/hormone receptors and enzymes/substrates which are currently used in affinity technology (Caro et al. 2006). Moreover natural biomolecules are low in abundance, unstable out of their native environment, can be difficult to integrate into industrial processes and also may not exist for a particular target molecule or difficult to synthesise as in the case of some small toxins. MIPs can potentially be synthesised to any target analyte with high affinity and selectivity mimicking the binding characteristics of antibodies, having additional benefits of stability, low cost, ease of preparation and chemical modifications without the use of animals (Canfarotta et al. 2016).

MIPs produced towards different molecules using different procedures can have different characteristics such as high surface area, soluble in water and the capacity to be made specific to a particular template which may enable them to be effective substitutes for enzymes and antibodies in sensors, catalysis and separation. MIPs have already been used for immunoassays and sensors for bioanalysis and as

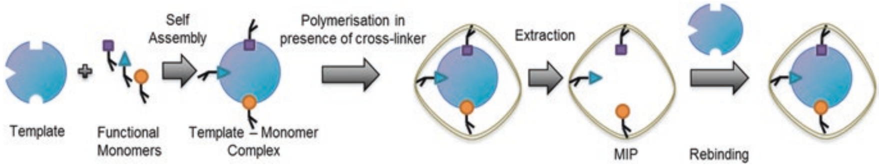

Fig. 8.1 Schematic of the molecular imprinting process (Abdin et al. 2015)

affinity separation materials. A big advantage of molecular imprinting is that it can be applied to a vast array of targets. Some of these include pharmaceutical products, amino acids, nucleotides, steroids, toxins and pesticides. Creating MIPs for small molecules is relatively straightforward as evidenced in the literature. However creating MIPs for large biomolecules, e.g. proteins, cells and microorganisms, remains a challenge. Proteins are specifically difficult to molecularly imprint. This is due to the properties of their three-dimensional structures. These structures are flexible, complex and change quite easily with minimal energy required to adjust their conformations. Also the imprinting conditions from solvent, pH, temperature and monomers ratios and composition need to be selected to ensure the production of the optimal MIP. Imprinting of compounds usually prefers a more rigid type of structure (Bossi et al. 2012). Attempts to directly imprint proteins have been documented in scientific research; however these attempts are limited to the cost of the generally expensive template proteins. To overcome these problems of imprinting large analytes as proteins or cells is the use of epitope imprinting. Epitope imprinting is the imprinting of only the epitopes (regions of molecules recognisable by affinity ligands) of the template protein or cells to create specific cavities which recognise and selectively bind to the analytes at these points (Nishino et al. 2006). These techniques are used largely in antibody production methods when synthesising antibodies towards specific sites on the protein or microorganisms. There are advantages in using this type of imprinting method. Epitopes for many protein molecules are known and easily accessible from crystal structure data and epitope mapping. These cavities bind specifically and selectively to the epitope regions of the proteins. The cavities are flexible enough to bind to the protein and maintain their conformation during the detachment of the protein molecule and the reattachment of another protein molecule. These cavities enable the protein target to bind in a particular orientation which allows greater control of the binding interaction and exposes other epitopes on the molecule which are free to bind to other ligands (if required). The creation and manufacturing of these cavities are relatively easy and inexpensive (Tai et al. 2010).

In imprinting large molecules such as proteins, microorganisms and cells, special considerations must be taken to ensure the creation of complementary MIPs (Li et al. 2014). Two major factors which affect the formation of complementary cavities are the uniformity of the pre-cross-linking mixture, and the release of the template after cross-linking is accomplished. If the polymer reagent and the template aggregate when combined together, the resultant 3-D polymer will have cavities which are complementary to these aggregate formations. This increases the nonspecific binding of the MIP and reduces its specificity to the target. The selectivity of the MIP also depends on the vacated complementary cavities. If the washing procedure is not effective at removing the template from the cross-linked hydrogel, then a recognition cavity would not be created to rebind the target. Therefore, a successful method needs to combine the prevention of aggregate formation prior to polymerisation and MIP cross-linking with the complete, effective removal of the templates from the MIP (Bolisay et al. 2007).

Several research groups have been able to produce excellent MIPs as nanoparticles with negligible aggregation and with acceptable levels of template removal (Guerreiro et al. 2009; Hoshino et al. 2010; Altintas et al. 2016a). Innovative technologies such as in vivo antibody mimicking nanoparticles and automated nanoparticle production are the current advances in this field. MIPs have lower manufacturing costs for industrial production when compared to antibodies. They are also more resistant to chemical and biological damage and inactivation than labile antibodies (Asliyuce et al. 2012). The removal of analytes using MIPs has various applications in medicine, veterinary care, agriculture, biopharmaceuticals and biological warfare. These MIPs can be placed in a purification column and act as 'sponges' to selectively capture target analytes but allow other nontarget molecules to pass through (Bolisay and Kofinas 2010). MIPs can also be produced in several physical forms like porous microspheres, nanospheres, nanostructure films and nanogels (Pichon and Chapuis-Hugon 2008).

8.3 Synthesis of Molecular Imprinting Polymer Nanoparticles

Molecular imprinting polymerisation is currently the focus of intense research interest and is being used in a wide range of application areas, e.g. in the preparation of selective separation materials, artificial (plastic) antibodies and synthetic enzymes. The first-generation MIPs were prepared by bulk polymerisation, resulting in monolithic polymers that necessitate grinding and sieving before use (Chianella et al. 2003; Lim et al. 2016). These ground MIPs typically have irregular shapes, are insoluble in any solvent and require exhaustive extraction for the removal of the template. These were mainly successful as solid-phase materials in column separation technology and as absorbers, but their application as sensing surfaces was hampered by the lack of specificity in real samples matrices. However, producing the MIPs in a nanomaterial format has reduced their nonspecific binding and increased their sensitivity and specificity towards their target template. Hence, the successful application of MIP nanoparticles as sensing materials in biosensors applications. Today submicron-size polymeric particles such as microgels, nanogels, microspheres and nanoparticles are fast becoming the format of interest in MIP production. NanoMIP particles are found to exhibit superior binding kinetics similar to antibodies and higher specificity due to their small structure and are easy to characterise since they are produced in solutions.

Molecular imprinting relies upon the presence of complementary interactions (non-covalent or reversible covalent) between sites in the template molecules (the analyte) and the functional monomer(s) used in the polymerisation process. The functional monomer(s) is a key component in the imprinting process, though generally constituting a relatively small percentage of the resultant MIP. The complexation of a template by these building blocks prior to, and during, polymerisation, to yield the complementary positioning of functionalities, is the central dogma of molecular imprinting. The monomers are held in place by cross-linking and copolymerised to form a cast-like shell. By removing the template, the binding site is exposed, and this can be used to rebind the analyte template with high selectivity. There are two major methods to achieve molecular imprinting to synthesising MIPs, which are the covalent and the non-covalent imprinting.

Covalent imprinting involves the functional monomers and template to bind through covalent linkage before polymerisation, and the template needs to be removed using chemical reactions. The MIPs then rebind to the target molecules using the same covalent interaction. Covalent imprinting allows very stable complexes between template and monomer to be formed; however the slow binding and release of template and difficulty in producing MIPs using this procedure are a limiting factor. Also any template not removed may leach into samples (Spivak 2005; Mayes and Whitcombe 2005).

Non-covalent imprinting is the most extensively used method of producing MIPs for three reasons:

– The process is relatively easier compared to the covalent methods, as it does not require synthesis steps for the pre-polymer complex as binding interactions between monomers and template take when mixed in solution.
– Removal of template can be extracted via several washings without the need for chemical reactions like the covalent method.
– The non-covalent procedure allows further functionality to be adopted into the MIP binding site.

The non-covalent method allows the formation of template and monomer complex in situ through non-covalent interactions such as hydrogen bonding, hydrophobic interactions, electrostatic forces and van der Waals forces (Madhuri et al. 2014). The template is easily extracted, and rebinding of the template and MIP is faster that also occurs through non-covalent interactions in comparison to covalent interactions. When producing molecularly imprinted polymers (MIPs), it is important to understand the nature of the template so that the correct functional monomers, cross-linkers, solvents and initiator can be selected and optimised. Also consideration must be given to the method of initiation and the duration of polymerisation (Whitcombe et al. 2011). After designing and developing the MIPs, different researchers apply the MIPs in a range of applications such as to replace biological molecular receptors, in chromatography and in solid-phase extraction or for immunoassays and biosensor development (Wulff 2013). This chapter will focus on the non-covalent procedure, as it is the method that is used in nanoMIP production.

8.3.1 Template

The template which is the analyte of interest or an analogue is crucial to the imprinting process as it is responsible for the self-assembly organisation of the functional monomers around the binding sites. Interactions between the template and the functional monomers will determine the recognition property of the produced MIP. For free radical polymerisation, the template needs to be stable to produce MIPs successfully. The template should not contain functionality that could stop or slow down the free radical polymerisation such as a thiol group. The template should be stable to at least 60 °C and contain active groups for the process to occur successfully (Martin-Esteban 2001). A wide range of template molecules (analytes/compounds) have been used to produce MIPs including recently many proteins, cells and microorganisms (Tothill and Turner 2003; Pichon and Chapuis-Hugon 2008).

8.3.2 Functional Monomers

The binding interactions in the imprinted cavities of the MIPs are made possible due to functional monomers. It is important to understand the function of the template so that suitable functional monomers can be chosen in a complimentary manner to maximise the complex formation during the imprinting process. It is normal practice to use excess functional monomers in non-covalent procedures usually 1:4 ratio or more to ensure the monomers assemble around the functional groups of the template. If more than one functional monomer is used, the reactivity ratio needs to be optimised for polymerisation to be feasible (Cormack and Elorza 2004). However, the use of high amount of functional monomers would result in nonspecific interactions, because of the overabundance of binding sites randomly distributed throughout the polymer (Li et al. 2016). Too low amount of functional monomers would lead to an insufficient molecular self-assembly, resulting in low selectivity. Therefore, only stoichiometric interactions between templates and monomers can be expected to produce the best selectivity. There are several acidic, basic, neutral and electrically charged functional monomers available commercially to facilitate the production of polymers in different conditions as shown in Fig. 8.2. To select the optimal monomers to be used for the synthesis of a MIP towards a specific target compound, a combined approach of computer (molecular) modelling and/or chemical affinity binding knowledge is used (Chianella et al. 2002); other more novel approaches have also been reported in the literature (Ashley et al. 2016).

8.3.3 Cross-Linkers

In molecularly imprinted polymers, cross-linkers have three important roles:

- Allows stabilisation of the imprinted binding sites.
- Control over the structure of the polymer matrix in different formats such as macroporous gel or microgel powder.
- Cross-linkers contribute to the mechanical stability of the polymer matrix.

The reactivity ratio of the cross-linkers should be matched to the functional monomers, and usually excess cross-link ratios over 80% are used to produce permanent macroporous material with mechanical stability. The ratio of cross-linker

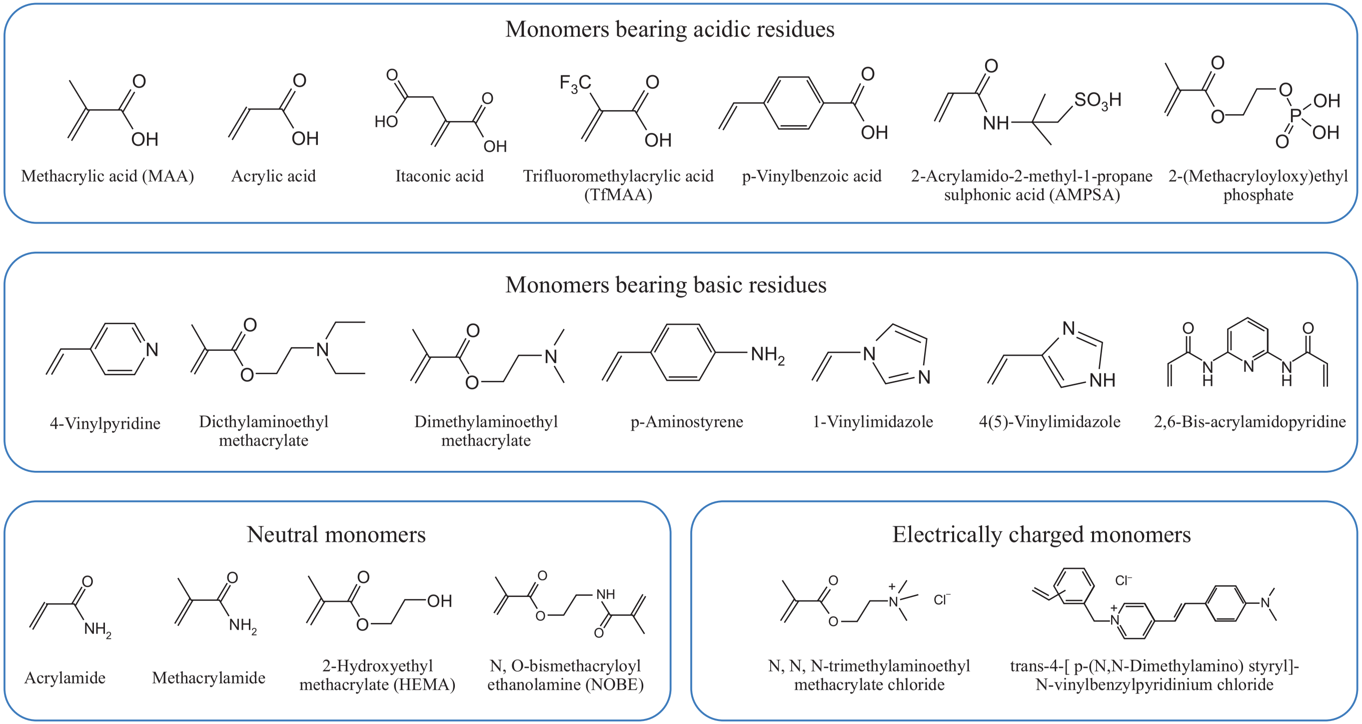

Fig. 8.2 Currently available monomers suitable to form a complex with a target molecule in acidic or basic conditions

can be estimated by studying the values of structural analogues. When using cross-linkers with multifunctional monomers, different vinyl groups can be incorporated into polymer at different rates; therefore the polymerisation reactions need to occur for a sufficient length of time (Cormack and Elorza 2004). A list of cross-linkers that are well known and compatible with molecular imprinting can be found in Fig. 8.3.

8.3.4 Solvent (Porogen)

The porogen has two roles, firstly to act as a solvent to bring together the template, functional monomers, cross-linker and initiator to allow interactions to occur in one phase. A suitable solvent needs to be chosen to increase the chances for the template and functional monomer complex to be formed. Apolar and non-protic solvents such as toluene allow the stability of hydrogen bonds. Moreover if hydrophobic interactions are required for the formation of template and functional monomer complex, water can be used as a solvent. Secondly, the porogen also acts as pore-forming agent when macroporous polymers are synthesised. The use of a thermodynamically stable solvent produces polymers with well-developed pores and highly specific surface area. The type and amount of porogen used can determine the overall structure and pore volume (Cormack and Elorza 2004). Other porogens that can be used are acetonitrile, chloroform and dichloromethane (Martin-Esteban 2001).

8.3.5 Polymerisation Techniques

There are several well-established techniques that are utilised to produce molecularly imprinted polymers. These are briefly listed in Table 8.1, with their advantages and disadvantages. Considerable research has been undertaken to synthesise MIPs with improved structure, functions and performance and enhance their specificity and sensitivity for application in the biosensor field. The solid-phase technique will be discussed in detail as it is a novel approach that provides significant advantages over existing techniques and is used to produce the nanoMIPs.

The solid-phase synthesis is a new method of MIP nanoparticles production (Ambrosini et al. 2013, Mazzotta et al. 2016; Canfarotta et al. 2016). In this procedure the template is immobilised onto silica beads so that the template is exposed at the surface for the functional monomer(s) to interact with the functional groups of the template. These beads can also be polymer resins, polysaccharide or a metal surface. The ability to immobilise the template onto silica beads ensures that the template is in a fixed orientation resulting in ‘monoclonal’ MIPs. The beads act as physical support to allow affinity separation of the MIPs from the template significantly reducing template leaching observed in bulk monolith procedures. Another significant advantage of using silica beads is that template remains on the beads for potential reuse depending on the stability of the template, making this approach very cost-effective. The process of MIP formation and affinity separation is

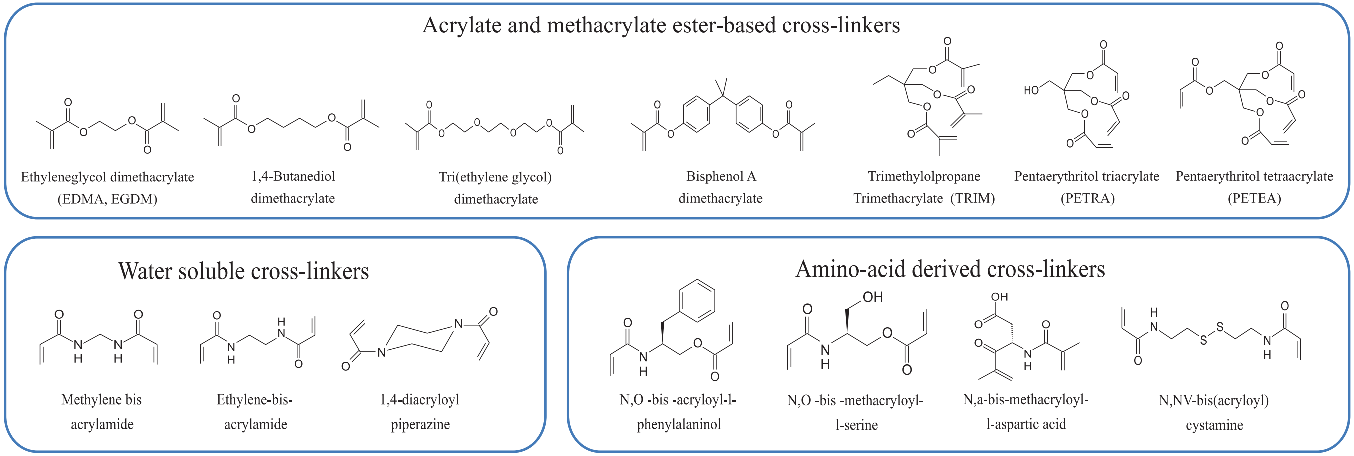

Fig. 8.3 Cross-linkers currently available for the synthesis of molecularly imprinted polymers (Modified from Cormack and Elorza 2004; Mayes and Whitcombe 2005)

Table 8.1 The advantage and disadvantages of other polymerisation techniques (He et al. 2007; Pichon and Chapuis-Hugon 2008)

Polymerisation method	Advantages	Disadvantages
Bulk monolith	Simple process and cheap	Poor chromatographic performance, time-consuming and low yield
Suspension	Suspension in water or perfluorocarbon produces high-quality MIPs 5–50 μm	Water incompatible with most non-covalent procedures and liquid fluorocarbons are expensive
Two-step swelling	The spherical particles uniformly packed with separating ability similar to bulk monolith with better chromatographic performance	Poor chromatographic performance
Dispersion	Can be used for water-soluble templates	Templates cannot be reused
Precipitation	Requires no surfactant with minimal optimisation required for polymerisation and good yield of high-quality MIPs	Binding sites present inside their network result in slow mass transfer of target molecules

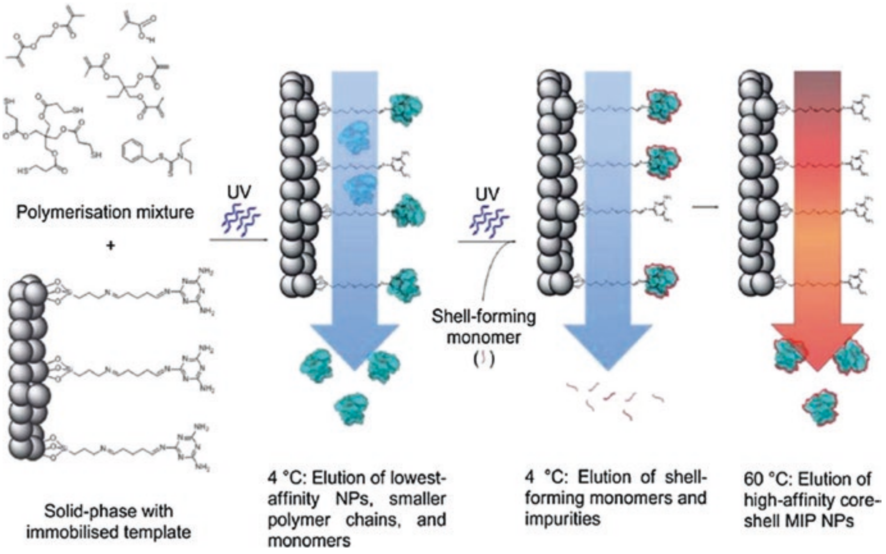

Fig. 8.4 Schematic of MIP formation around immobilised template and temperature-based affinity separation (Moczko et al. 2013)

displayed in Fig. 8.4. There are two polymerisation methods that can be used, the chemical synthesis and the UV photopolymerisation.

The chemical synthesis method was developed by Hoshino et al. (2008). This method uses water as a solvent and is appropriate for targets such as

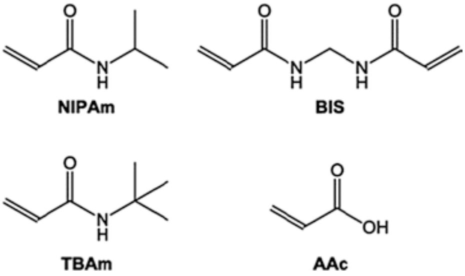

Fig. 8.5 Monomers used to prepare MIP nanoparticles

bio-macromolecules that may denature or undergo changes in their structure when in organic solvents such as acetonitrile. Monomers used for polymerisation include *N*-isopropylacrylamide (NIPAm), *N*-tert-butylacrylamide (TBAm) and acrylic acid (AAc) and act as functional monomers. The monomer *N*,*N′*-methylenebisacrylamide (BIS) is used as a cross-linker, and the chemical structures are shown in Fig. 8.5. An additional monomer is used, *N*-(3-aminopropyl)methacrylamide hydrochloride (APS), to provide primary amine groups to the surface of the MIP for surface immobilisation purposes. The chemicals ammonium persulfate and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TEMED) are used in combination as an initiator (Hoshino et al. 2008; Hoshino and Shea 2011).

The other method is the UV photopolymerisation method which requires an organic solvent for the MIP production to occur. The process of this polymerisation is known as the living radical polymerisation where it is controlled through the selected iniferter, which consists of nitroxide-mediated polymerisation (NMP), atom transfer radical polymerisation (ATRP) and reversible addition-fragmentation chain transfer polymerisation (RAFT). Iniferter such as *N*,*N*-diethyldithiocarbamic acid benzyl ester acts as the initiator, transfer agent and the terminator hence the name ini-fer-ter. An initiator of this type decomposes reversibly to a pair of free radicals. One of the free radicals is the active propagating species, and the other is less reactive, acting as the transfer agent and termination of the polymer chains, while also reforming new initiating species (Sulitzky et al. 2002; Poma et al. 2010). The process is highlighted in Fig. 8.6. The significance of this process is the ability to control the rate of polymerisation and to be able to undergo another polymerisation step by reapplying a UV light source. The iniferter moieties will remain present in the MIP allowing surface modifications such as adding primary amine group or PEG shells while retaining the integrity of the binding site as the presence of the template prevents further changes in the cavity (Rückert et al. 2002).

Soluble and stable MIP nanoparticles are produced at the end of the polymerisation procedure. The next step involves the elution of low-affinity particles removed by cold washes at 0 °C and the elution of high-affinity particles with washes at 60 °C as previously stated in Fig. 8.4.

Surface imprinting techniques are attempting to address the concerns and challenges of imprinting larger molecules also as proteins, cells and microorganisms. There are two main types which are indirect and direct imprinting. Each type has a variety of examples further illustrating the non-standardisation of MIP imprinting. Directing

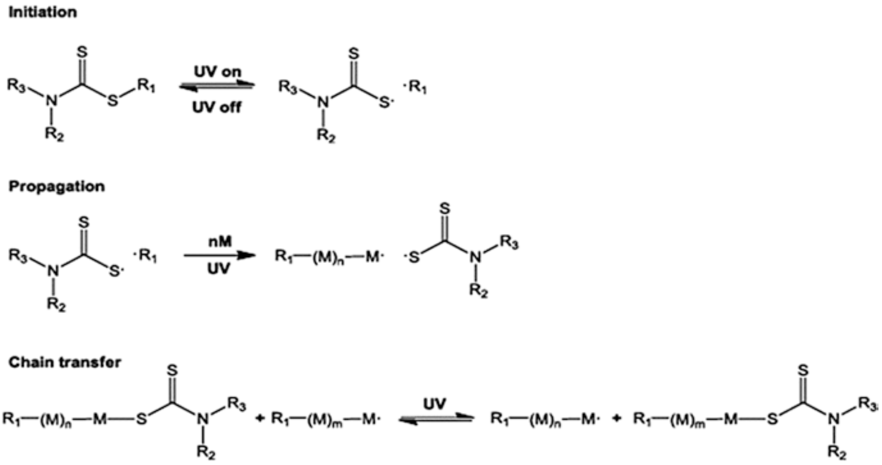

Fig. 8.6 The schematic of the iniferter polymerisation mechanism (Poma 2012)

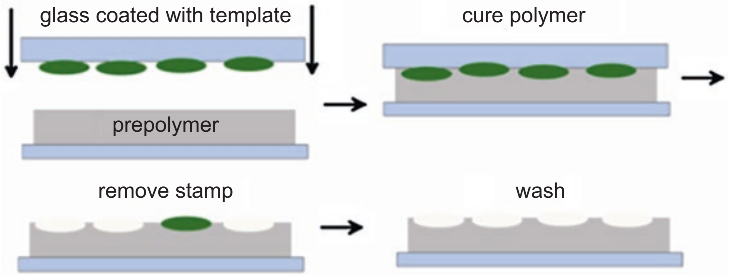

Fig. 8.7 Stamp imprinting (Schirhagl et al. 2012)

imprinting is generally easier and therefore more popular. Stamp coating is an example of direct imprinting and is common because it is easy and flexible (Schirhagl et al. 2012). The target analyte is placed on small 3–8 nm stamps or glass slide. The solvent is then removed through drying or spin coating. Spin coating is sometimes required to remove excess buffer which can form problematic crystals on the template. The stamps are then pressed into the pre-polymer to make an impression. The viscosity of the pre-polymer must be appropriate for a proper imprint to be made. The removal of the template from the cured polymer creates the recognition site (Fig. 8.7).

Indirect imprinting methods are used when the template is live cells or high-risk dangerous analytes (e.g. pathogenic), unstable or very large. Artificial template stamps are used for large complex templates such as cells in a double imprinting method which allows for high reproducibility of the artificial template. The natural target is imprinted into the polymer and removed. The resultant cavity is with a second pre-polymer mix which forms the artificial template. The polymers are

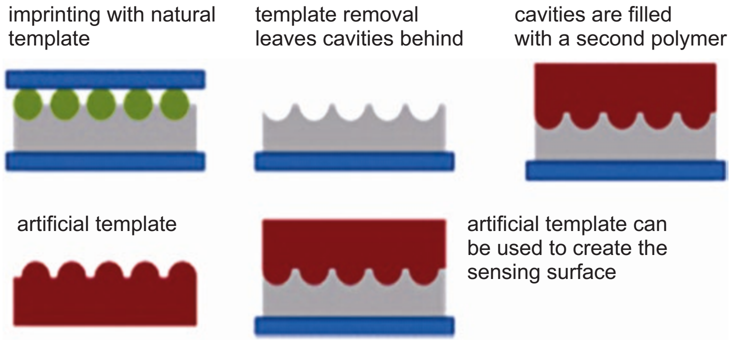

Fig. 8.8 Indirect imprinting (Schirhagl et al. 2012)

separated, and the artificial replica can be used to create specific cavities in a separating imprinting step (Fig. 8.8).

8.3.6 Molecular Modelling

Producing bioaffinity ligands such as MIPs and then manually testing different combinations can be a time-consuming process. Using molecular modelling for MIPs to identify possible combinations of functional monomers can prevent unnecessary experiments preventing waste of materials. Most importantly it can help to identify potential monomers that bind with high affinity to the template.

Molecular modelling is a powerful tool to study molecular recognition, the specific interaction between the analyte and the constructed receptor. The affinity interactions between synthetic receptors and target analytes comprise hydrogen bond interactions, p-stacking interactions, van der Waals interactions and electrostatic interactions, which constitute molecular forces involved in molecular recognition processes. To design the artificial receptors, computer modelling is used to provide structure information for the target analyte, which will then be used to guide the design of combinatorial libraries and rational design of the artificial receptors. Molecular modelling allows the prediction of ligands that are expected to bind strongly to key regions of biologically important molecules (e.g. enzymes, macromolecular receptors) of known three-dimensional structure, so as to inhibit or alter their activity (Tothill and Turner 2003).

Choosing the right monomers for a template with a two-component combination of a 100 monomers, 5000 polymers need to be produced and tested which is a monumental task (Karim et al. 2005). The task becomes more complicated when factors such as the ratios of monomer, cross-linker, template and also the solvent need to be determined. Thermodynamic calculations on multicomponent systems would be extremely difficult and time-consuming requiring a lot of resources.

By simplifying the parameters to just focus on the monomer(s) and template using molecular modelling software, thermodynamic calculations can be carried out and reduce computational time. SYBYL uses the Leapfrog™ algorithm to screen a template with a virtual library of the 21 most commonly used monomers to identify the monomer(s) with the highest binding score. The score will indicate the best potential monomer, and final annealing simulations are carried out to obtain the optimised arrangement of the functional monomers around the template. However it must be noted that as the reactivity ratio and the solvent are not taken into account, it could potentially produce polymers with no affinity to the template. The computation approach was used by Chianella et al. (2006) successfully in selecting monomers for abacavir with high affinity. Altintas et al. (2016a, b) used computational chemistry to select monomers for pharmaceuticals and endotoxins imprinting. Using SYBYL to identify functional monomers for target analytes can save time and materials by ruling out non-suitable monomers preventing unnecessary experiments. Molecular modelling can also potentially identify a combination of monomers that have not been tried before in literature for a template.

Very recently a novel technique has been introduced to select the monomers, and this is based on the use of differential scanning fluorimetry in the rational design of MIP nanoparticles for protein targets (Ashley et al. 2016).

8.4 Application of MIP Nanoparticles in Biosensors and Diagnostics for Food Application

A biosensor is an analytical device incorporating a molecular recognition material, a biologically derived material or a biomimic, which is either associated with or integrated with a physicochemical transducer or transducing micro-systems. The usual aim is to produce a digital electronic signal that is proportional to the concentration of a specific analyte or group of analytes (Tothill and Turner 2003). There are many types of transducers that can be used in a biosensor device, and these mainly include electrochemical, optical, mass-sensitive, calorimetric, magnetic and micromechanical transducers. More recently the analytical capability of these devices has been further increased through miniaturisation and advancement in microelectronics as well as the incorporation of nanomaterials in their design and manufacture. As the transducer technology is developing rapidly, the sensing elements that can be used in these devices is also expanding due to nanotechnology advances.

Recent developments in receptor discovery such as the development of artificial receptors known as biomimics have enhanced the stability of biosensors and opened up new application arena for their use (Justino et al. 2015). The use of molecularly imprinted polymers for application in the food analysis and environmental monitoring is expanding (Chen et al. 2011). MIPs are a popular recognition element for separation technology as well as for biosensors and diagnostics. There is a wide commercial interest for MIPs, particularly in solid-phase extraction of samples, and today there are few companies marketing these products such as Sigma-Aldrich and POLYINTELL, France. In this case their use is mainly for extracting the analyte from the complex environmental or food samples before conducting the analysis using other lab-based systems or ELISA methods. MIPs have been used to develop

ELISA type of kits. Chianella et al. (2013) conducted a direct replacement of antibodies with molecularly imprinted polymer nanoparticles in ELISA as a novel assay for pharmaceuticals detection such as vancomycin. Furthermore a wide research is being conducted to use MIPs in lateral flow assays to replace antibody. However, there are still some challenges which still have to be overcome to produce commercial lateral flow assays based on nanoMIPs technology.

The use of nanoMIPs in biosensors is having positive impact on the technology. MIPs can be used in conjunction with a variety of transducers and result in the formation of biosensors with excellent signal-to-noise ratio when optimised and also high-stability sensors. Assays have to be optimised and signal generation amplified for the sensitive detection of the target analyte. These devices can be used for food analysis on-site or at the farm or the factory. Many nanoMIPs have been developed for small molecules as environmental pollutants and toxins. One of these is endotoxins (lipopolysaccharides (LPS)) which are found on the cell walls of most gram-negative bacteria and some cyanobacteria. Endotoxins in drinking water pose a potential concern (Ogawa et al. 2012; Can et al. 2013). Therefore, there has been a need to develop high-sensitivity sensor towards endotoxins. Figure 8.9 shows the

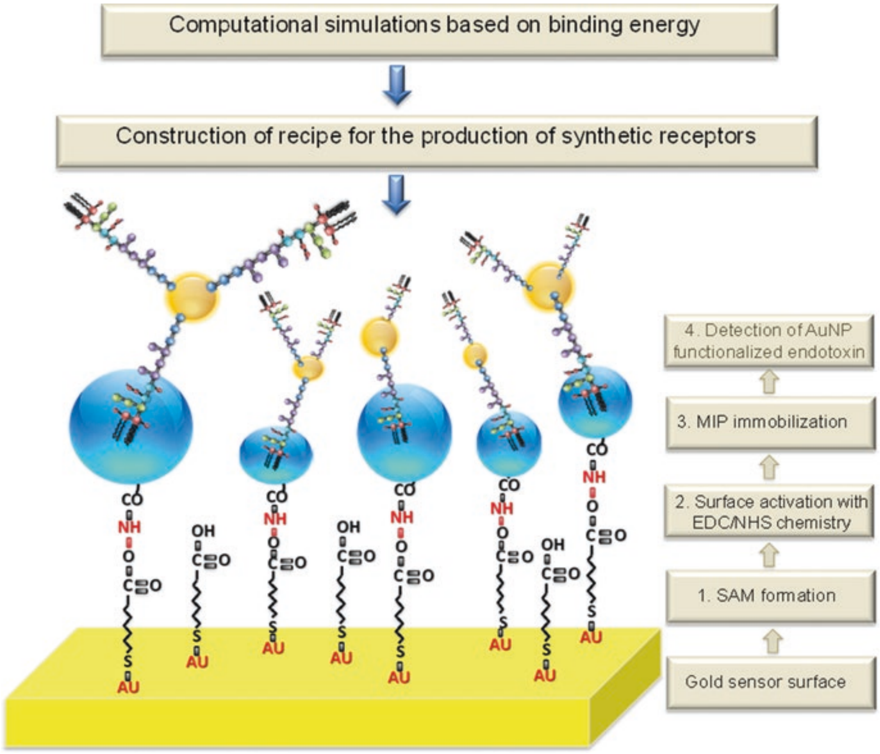

Fig. 8.9 Experimental design of entire research work from computational design of MIP receptors to affinity-based AuNP-functionalised endotoxin assays on the nanoMIP-immobilised sensor (Altintas et al. 2016b)

concept of constructing a sensor device where the recognition material is a MIP nanoparticle immobilised on the surface of a sensor platform developed for endotoxin detection (Altintas et al. 2016b). This sensor which was based on surface plasmon resonance (SPR) was able to detect endotoxins at 0.44 ng mL^{-1} with the aid of new sample preparation technique which was developed using trimethylamine. Furthermore these MIPs for the endotoxin can be regenerated and reused more than 30 times without significant decrease in binding response allowing the use of one sensor several times.

MIPs can be engineered to be selective to analyte shape as well as analyte surface chemistry. This allows for high specificity which can readily distinguish between very similar molecules, a significant advantage in biosensors. Lithographic production of MIPs coupled with QCM transducers leads to the production of very good sensor systems (Jenik et al. 2009). Sensors are critically important because they aid public health strategies, investigate outbreaks and aid prevention strategies. Smart materials and nanoparticles will greatly increase the potential of biosensors and make them more advanced. It would also aid the mass production of these devices and further enable reliable, accurate analysis to occur in real time at the point of sampling.

Unfortunately there are no standardised rules or guidelines for selectively imprinting large biomolecules such as proteins. These large biomolecules also have poor rebinding efficiencies to the created cavities. However MIPs remain heavily versatile recognition elements which are being used more increasingly in the production of biosensors. These devices can be designed for single use, reusable for multiple analytes or continuous monitoring. Nowadays sensors can be designed to handle the sample through the inclusion of a microfluidic system or membrane separation system as part of their design for extracted food sample handling. Viruses are a very important cause of a number of harmful diseases; therefore quick, selective and specific detection is critical for providing an appropriate response to environmental contamination such as water and also in food. Biosensors are the fastest-growing technology for the detection of viruses (Kleo et al. 2011). The targets are viral proteins, viral nucleic acids or antibodies produced by the host as a result of viral infection. Therefore successful incorporation of bio-receptors is critical to biosensor operation for water-borne diseases (Caygill et al. 2010; Altintas et al. 2015b). The final end game is the development of sensors which can efficiently identify and quantify the presence of a virus in a water sample in an easy, quick, sensitive and inexpensive manner. Viruses can also be found in food as contaminants of fruits and seafood. Current conventional techniques require approximately up to several days for molecular techniques and cost several hundred dollars per analysis, whereas a biosensor-based method can be factors cheaper (Yadav et al. 2010) and detect the presence of a virus in a water sample in an easy, quick, sensitive and inexpensive manner. Success of these technologies depends on improving the affinity, specificity and mass production of the molecular recognition components. In our work we designed and synthesised nanoMIPs for the detection of viruses, such as the bacteriophage MS2 and adenovirus (Altintas et al. 2015c, d). Both MIPs were produced using the solid-phase methods and had particle size around the 250–300 nm. The MIPs showed good sensitivity and selectivity towards the imprinted virus and very comparable performance as the antibodies when used to develop SPR-based sensors. Currently we are developing nanoMIPs towards allergens for application in the food production industry. These MIPs are also showing superior properties and performance in a food manufacturing setting. Detection of drugs of abuse is another area of huge interest, and many groups are developing MIP nanoparticles for use on either QCM-based sensors or impedance spectroscopy (EIS)-based sensors (Fernandes et al. 2015).

8.5 Future Outlook and Concluding Remarks

The food industry processes large quantities of raw materials and processed food and drink products with different characteristics and diverse qualities. Much of these materials can be contaminated with environmental pollutants, chemical used during the production process, and microbial contaminants and their toxins. Diverse populations and migration of people is placing further challenges for companies to be able to deliver food products for different markets at the same time. Therefore, ensuring safety and quality control practices is adhered to in the food industry is paramount. Hence advances are taking place to deliver diagnostics and sensors that can stand these challenges and deliver the type of sensors which can work in complex and difficult matrices. Applying nanomaterials in biosensors and diagnostics is advancing the technology and further their potential use. Molecular imprinting polymers have been mainly used as selective adsorbents, separations and solid-phase extraction in the diagnostic field with products that can now be found in the commercial market. The future outlook for MIPs now is their increased use and application in the sensors and diagnostics assay as well as biocatalysts. This has come about with the huge development which is taking place in the design and synthesis of nanoMIPs and the incorporation of man-made transitional metals and smart polymer synthesis. These sophisticated methods of synthesising the new generation of MIP nanoparticles and MIP nanofilms are paving the way for the increased use of these smart nanomaterials in the diagnostics arena. The use of nanoMIPs as the biomimics to replace biomolecules as the sensing materials will increase the stability of the devices and their shelf life and reduce the cost of production. Biosensor systems, which are relatively small portable instruments, have an on-site application, and their relatively low cost is clearly desirable. This will increase the application of biosensor in the food, agriculture, veterinary diagnosis and environmental testing in the developed as well as developing countries to ensure quality and safety.

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Nanotechnology Applications in the Food Industry

9

Emmanuel A. Echiegu

Abstract

Nanotechnology is the study, creation and use of materials, devices or systems at the extremely small scales of 1–100 nm where novel phenomena and properties of mater, which differ significantly from that of the bulk materials, are known to arise. This is largely because of the larger specific surface area which gives rise to the exhibition of quantum effect. This phenomenon has given rise to novel application of the technology in various domains of knowledge including agriculture, biotechnology, medicine, materials science, etc. In the industry of food processing, packaging, storage and distribution, nanotechnology is employed in the incorporation and targeted delivery of nutrient in food and in enhancing the bioavailability of the nutrient. It is also employed in the introduction of antimicrobials and health supplements and in tracking of contaminants in food among other uses. Nanomaterials used for various purposes in the food industry include nanoparticles, nanofibres, nanotubes, nanoemulsion, nanoclays, nanocomposites, nanocapsules, nanosensors, etc. Presented in this chapter are the materials, structures, systems and processes involved in processing, preservation, packaging, handling and storage of food for enhanced food quality and food safety. Potential hazards associated with the use of nanotechnology in the food industry as well as needed regulatory measures are also discussed.

Keywords

Nanotechnology • Nanomaterials • Nanoparticles • Nanocomposites • Nanoemulsions • Nanofibres • Nanotubes • Nanosensors • Nutraceuticals • Food industry • Food processing • Food packaging • Food safety

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9.1 Introduction

Nanotechnology is the study, design, creation, manipulation and use of materials, devices or systems at the extremely small scales of 1–100 nm where novel phenomena and properties of mater are known to arise (Ravichandran and Sasi Kala 2006, Alfadul and Elneshwy 2010, Ravichandran 2010, Singh et al. 2015, Echiegu 2016). These properties can be physical, chemical, electrical, mechanical, optical or magnetic. The novel properties are largely due to the fact that nanosized materials have significantly large specific surface areas. Since chemical and biological reactions are surface phenomenon, the larger surface area relative to the volume results in greater reactive activities when compared to bulk materials of similar chemical composition (Alfadul and Elneshwy 2010).

Nanotechnology has found applications in various disciplines such as medicine, biotechnology, agriculture, biological sciences, etc. (Tarver 2006; Ravichandran 2010). In agriculture it is employed for rapid detection and molecular treatment of diseases. It is used for enhancing bioavailability of plant nutrient. Various viruses and pathogens are now being tackled in the agricultural industry using nanosensors and smart delivery systems. The application of nanotechnology leads to a reduction in the quantity of agrochemical and fertilizers used in crop production. Targeted delivery of these agrochemicals minimizes the problem of wastage as a result of leaching, degradation by light or microbial action. Nanotechnology also enhances the efficacy of pesticides, herbicides and other agrochemicals leading to the use of smaller dosages and, hence, the reduction of environmental problems usually associated with their use (Joseph and Morrison 2006; Prasad et al. 2014, 2017; Singh et al. 2015).

Nanotechnology application in food processing, packaging and distribution is a fairly recent innovation although steady and rapid progress is being made in this sector. The technology has given rise to the development of food with greater bioavailability and improved shelf life by incorporating functional and more readily available elements in food. It is also applied in tracking of contaminants in packaged food and in the introduction of antimicrobials and health supplements (Neo et al. 2013; Pradhan et al. 2015).

In applying nanotechnology in the food industry, various nanomaterials and structures are utilized. Presented in this chapter are the materials, structures, systems and processes involved in processing, preservation, packaging, handling and storage of food for enhanced food quality and food safety.

9.2 Nanosystems

These, in the context of this write-up, refer to the types and forms of nanomaterials employed in the food industry. Nanomaterial is any natural or artificially created material containing particles in unbound state in which at least one of the external dimensions in the range of 1–100 nm (The European Commission 2011; Sekhon 2014). It includes nanoparticles, nanofibres, nanocapsules, nanotubes, nanoclays, nanofilters, nanocomposites, nanoemulsions, nanosensors, nanobarcodes, etc. (Duncan 2011).

9.2.1 Nanoparticles

These are naturally occurring or anthropogenically created nanosized particles which are known to impart some desirable properties when incorporated in food. Since nanosized materials have large specific surfaces, a very large percentage of the atoms exist at the surface compared to bulk materials; and this gives rise to quantum effects.

Nanoparticles are classified as hard or soft. Hard nanoparticles include titanium oxide, silica and fullerenes (i.e. nanoparticles having hollow or tubular molecules), etc. Soft nanoparticles include liposomes, vesicles, nanodrops, etc. Some nanoparticles employed in the food industry in industrial scale include:

- *Nanosilver*: This nanoparticle typically measures about 25 nm. It is the most studied and utilized nanoparticle in food and pharmaceutical industries. Nanosilver has strong inhibitory and bactericidal properties (Wang et al. 2007; Alfadul and Elneshwy 2010; Singh et al. 2015). By suppressing respiration and transport of substrate through the microbial cell membranes among other ways, silver nanoparticles inhibits microbial growth (Nanosilver Manufacturing SDN BHD 2014). Nanosilver is highly stable, safe, efficacious, non-allergic and hydrophilic. They are employed in food packaging and as health supplements in food. By absorbing ethylene produced during the process of fruit ripening, nanosilver helps to extend the shelf life of perishable crops since ethylene hastens the deterioration of fruits and vegetables.
- *Zinc oxide:* This antimicrobial agent impedes the flow of oxygen into or out of packaging containers (Pradhan et al. 2015) therefore minimizing deterioration. It is therefore used for food packaging and as nutritional additives (Brunner et al. 2006).
- *Titanium dioxide* (TiO_2): This non-toxic nanoparticle is used in food products at up to 1% of the final weight (Singh et al. 2015). Compared to chlorine or ozone, this antimicrobial agent is a very strong disinfectant. It is used for food preservation, food packaging and storage containers and as nutritional additives (Brunner et al. 2006; Long et al. 2006; Alfadul and Elneshwy 2010). The photocatalytic effect of this nanoparticle makes it particularly useful for food packaging that requires the blockage of ultraviolet radiations. It is also used as whitener for dairy products such as milk and cheese (Pradhan et al. 2015).
- *Silicon and carbon nanoparticles:* These anti-caking agents have the property of reducing leakage of moisture. They absorb moisture in food making them very favourable for hygroscopic application. Silicon nanoparticles can also be used as food colourant, food additives and for food packaging (Chen and von Mikeez 2005).
- *Platinum and gold nanoparticles:* These nanoparticles are employed in the development of biosensors used to improve food analyses (Wang et al. 2007), among other things.
- *Inorganic ceramic:* This is used in food packaging and preservation and in cooking oil for deep frying as will be explained later.
- *Polymeric nanoparticles:* These are efficient delivery system and bactericide used in food packaging and preservation.

9.2.2 Nanofibres

Nanofibres are usually made of polymers and are used for controlled and targeted delivery of nutraceuticals and other bioactive materials. Their use in this manner leads to significant improvement in bioavailability, especially for poorly soluble nutrients (Vasita and Katti 2006; Elmarco.com 2015). Nanofibers are also used to make sensors that change colour as they absorb chemical vapours. Such sensors can be used to show when the absorbing material becomes saturated with the absorbed vapours (Understandingnano.com. 2016).

9.2.3 Nanotubes

These are nanoscale, tube-like structures which belong to a family of nanomaterials known as fullerene. Fullerenes are hollow structures with their walls formed by one-atom-thick graphene. Carbon nanotubes (CNTs), an allotrope of carbon, are the most commonly used in the industry of food processing, packaging, preservation, storage and distribution. This is because of their extraordinary strength, unique electrical and efficient thermal conduction properties (Varshney 2014; Science Daily 2016).

9.2.4 Nanoclays

These are naturally occurring stable, eco-friendly, layered aluminium silicate nanoparticles. Nanoclays are used in the production of clay nanocomposites – a hybrid polymer-clay nanomaterial which can be used as rheological modifiers, gas absorbents and bioactive materials delivery carriers (Sigma-Aldrich 2016).

9.2.5 Nanocomposites

Nanocomposite is a solid combination of two or more materials with dissimilar structures and chemistry and hence differing properties. One of the component materials forms the bulk matrix, while the other(s) serves as the reinforcement. The reinforcement materials are finely and uniformly dispersed within the matrix material. The matrix material may be ceramics, metals, etc. In the food industry, however, the most popular matrix material is polymer. The reinforcing material may be nanoparticles such as minerals, exfoliated clay stacks, molybdenum disulphide, tungsten disulphide, etc. Nanofibres such as CNTs can also be used as reinforcing agent.

Nanoclay-polymer composites have high barrier properties; it provides improved protection against migration of chemical agents across barriers (Hegde et al. 2005) and therefore helps in keeping food products fresh and free from microbial and other infestations for a reasonable length of time.

9.2.6 Nanoemulsion

When two or more liquids such as oil and water, which do not readily combine, are mixed together, the result is an emulsion (Ravichandran 2010). Nanoemulsions are liquid-in-liquid dispersions with droplet sizes on the order of 100 nm. Compared to conventional emulsions, nanoemulsions are highly stable. They cannot be easily separated by gravitational forces due to their small particle size. Separation through the aggregation of the droplets is also not easy since the droplets are usually coated with surfactants which inhibit them from coalescing due to interfacial repulsion.

In the food industry, nanoemulsions are used for salad dressings, ice creams, etc. With the small particle size, the products are creamier. They are also very easily transported across epithelium of the digestive system and therefore enhance adsorption of the components better than other emulsions. Nanoemulsion has a wide range of activities against pathogenic and non-pathogenic microorganisms (MNIMBS 2010).

9.2.7 Nanocapsules

Nanocapsules usually consist of a non-toxic polymeric shell which encapsulates a hollow cavity that can contain active nanoscale substances in liquid or solid form or in form of a molecular dispersion. They are easy to handle, stable and protect encapsulated bioactive ingredients from adverse environmental conditions. They also mask taste. The release of the encapsulated active ingredient may be triggered by moisture, temperature or pH (Marsh and Bugusu 2007; Ezhilarasi et al. 2012). The active ingredient can also be delivered to a specific target at a specific time in the biosystem, resulting in enhanced bioavailability.

9.2.8 Nanosensors

Nanosensors are nanostructures designed to detect changes in colour of food and/or the presence pathogens and other microorganisms, among other things. They are also used to detect the presence of volatiles produced during spoilage (Fernández et al. 2008). Such gases include ammonia, hydrogen sulphide, sulphur dioxide, etc. Apart from detection of changes or presence of contaminants, nanosensors are also used in monitoring and control, quality assurance, etc. (Kempers 2009). Nanosensors are highly sensitive and are thus more efficient than conventional sensors.

Nanosensors can be metal based such as palladium, platinum and gold (Guma-Diaz 2010; Wei et al. 2010). Metal-based sensors are used in the detection of any changes in the colour, light, heat, humidity or chemical composition of the food. They are also used in the detection of toxins or the presence of any gases produced as a result of spoilage (Kang et al. 2007; Meetoo 2011). Volatile organic compounds such as ethylene, ethanol, CO, etc. are detected using nanocomposites of SnO_2, micro rods of titanium oxide and SnO (Mousavi and Rezaei 2011). The presence of residual pesticides on the surface of fruits and vegetables is detected using single-walled CNTs (Sozer and Kokini 2009), while the presence of carcinogens in food materials, food-borne pathogens and other microorganisms that usually infest food may be detected using carbon black and polyaniline (Yuan et al. 2008; Vidhyalakshmi et al. 2009; Biswal et al. 2012). Other biosensors such as electronic noses, nano-test strips and nano-cantilevers are used to detect changes in colour when they come in contact with food materials exhibiting signs of spoilage (Biswal et al. 2012). Other sensors are designed to accurately detect and separate genetically modified food (Kempers 2009).

With nanosensors-based pathogen indicators, the incubation period required for the accurate detection of the pathogens is highly reduced (Pradhan et al. 2015) leading to a more timely intervention to reduce losses and avoid spread and consumption of contaminated food.

9.3 Food Processing

Food processing is the practice of conversion of raw food ingredients into consumable, preserveable, transportable and marketable food and food products. The process includes the removal of toxins and protection of the food from pathogenic and other microbial infestation which lead to spoilage. It also includes the improvement of the consistency, flavour and quality of food (Chellaram et al. 2014).

Various food processing and preservation methods aimed at retarding or stopping the multiplication of microorganisms have evolved over the years. These include drying, fermentation, salting, roasting, cooking and oven-baking. Others are smoking, steaming (blanching), curing, pickling, refrigeration, caning, bottling, jellying, etc. (Pradhan et al. 2015). Despite the fact that the application of nanotechnology in food processing and preservation is a fairly recent innovation, rapid and steady progress has been made.

Nanotechnology is applied in food processing to deliver nutrients, increase bioavailability and potency, effect timed and targeted release of nutrients, mask undesirable taste and odours, protect sensitive nutrients, increase solubility and improve rheological and anti-caking properties. It is also applied in the creation of functional, interactive and multicomponent foods and to improve flavour and texture and enhance shelf life of food.

Nanocapsules are commonly employed in the delivery of nutrients in food. The encapsulated sensitive bioactive materials, which may be in in form of liquid, solid or molecular dispersion, are protected from unfavourable environmental conditions. The nutrients may be released through the process of hydration of the nanocapsule which causes the polymeric shell to swell and stretch thereby allowing the encapsulated bioactive material to diffuse through the polymeric membrane into the biosystem. The release may also be as a result of reactions between enzymes produced by the human body and the polymeric shell of the capsule which causes it (the polymeric shell) to rupture and release the encapsulated nutrient (Nagavarma et al. 2012).

Use of nanoemulsion is also very vital in the development of functional nanofoods. Usually particles less than 80 μm cannot be seen with the naked human eye, while those less than 40 μm cannot be sensed by the mouth (Aguilera 2009). Food elements that exist in nanoscale are not noticed because they are less than 80 μm in size and are therefore not visible to the naked eye. They are also not perceptible to taste because they are less than 40 μm in size. Food elements in form of nanoemulsion therefore do not change the organoleptic perception of the food item to which they are added because of their nanoscale size. Nanoemulsion also has the advantage over conventional emulsion due to their reduced size which provides larger surface area resulting in increased rate of adsorption.

9.3.1 Efficient Nutrient Delivery with Enhanced Bioavailability

Nutraceuticals are substances that are incorporated in food to enhance nutritional value of the food. Food supplements in form of nanoparticles or nanostructures (nanocapsules, micelles, liposomes, nanocochleates, etc.) are more effective than common supplements because their very small size enhances their absorption into the blood stream leading to increased bioavailability. Their larger specific surface area also results in increased bioactivity, greater potency and hence reduction in the quantity of additive need for a given level of chemical reactivity (Mozafari et al. 2006, Alfadul and Elneshwy 2010).

Nanoemulsions are commonly used for the delivery of phytochemicals (Pradhan et al. 2015). These plant-based chemicals are usually not readily available in biosystems. The use of nanoemulsion as a delivery system leads to improved bioavailability (Chau et al. 2007; Fernández et al. 2008; Bugusu et al. 2009; Pradhan et al. 2015).

9.3.2 Development of Interactive and Functional Foods

Some foods, known as interactive foods, respond to bodily requirements and so deliver nutrients more effectively. These are achieved through the process of encapsulation. Such "on-demand" food can remain dormant in the body and deliver nutrients to the cells only when needed (Joseph and Morrison 2006). The release can be triggered by changes in temperature, moisture or pH in the biosystem. Others known as "smart food" remain dormant but deliver nutrients only in response to deficiencies in the cells detected by nanosensors ingested with the food. Other smart products being developed include drinks that change colours and flavours in response to consumer's preference and foods that can recognize the nutritional needs or allergies of the consumer and adjust accordingly to suit their needs (Ravichandran 2010).

Development of functional food is another area in which nanotechnology is being employed. Functional food is defined as "a natural or processed food containing bioactive health-giving additives with clinically proven health benefits and which aids specific bodily function" (Lordan et al. 2011). It is important in the prevention, management and treatment of chronic diseases. Functional food, engineered through nanotechnology, can be used to intelligently manage weight loss. For example, by decreasing the particle size in the emulsion that gives ice cream the creamy texture, the specific surface area of the emulsion is increased resulting in enhanced bioactivity and hence reduction in the quantity of the emulsion needed to achieve the same level of creamy texture (Joseph and Morrison 2006). The fat content of the ice cream is thus reduced while achieving the same desirable creamy result.

Nanoencapsulated phyto-steroids such as lycopene, betacarotenes, etc. are now being used to replace meat cholesterol giving rise to healthy foods capable of preventing the accumulation of cholesterol in the body (Mozafari et al. 2006, Ravichandran 2010). Also some nanosized structural lipids have been developed to inhibit diffusion of cholesterol from the digestive system into the bloodstream (Dingman 2008; Chellaram et al. 2014), leading to less accumulation of cholesterol in the blood with its attendant health risks.

Layering concept is also being used to create food with unique functionality. Food in form of multilayered nanoemulsion can be designed with each layer having a unique function such as antioxidant, antimicrobial, moisture barrier and other functions (Weiss 2009).

9.3.3 Masking of Undesirable Taste and Odour

Undesirable taste and odour of some desirable nutrients can be masked through encapsulation and addition of the nutrient in the food. Such nanocapsules are designed to burst and release their content only when the nanocarrier reaches the stomach, thus avoiding the unpleasant taste and odour of such food in the mouth. For example, tuna oil which is high in Omega-3 fatty acids but has an unpleasant taste, has been incorporated in encapsulated form in bread. The encapsulation prevents the taste of the oil from being detected in the mouth, while the fish oil is released only during the digestion process in the stomach (Mozafari et al. 2006; Alfadul and Elneshwy 2010). Similar techniques are also employed in the formulation of yoghurt and baby foods to mask undesirable tastes or odours of some of the added nutrients (Mozafari et al. 2006).

9.3.4 Protection of Sensitive Nutrients

Nanotechnology also serves to protect sensitive nutrients and other bioactive materials through the use of nanoencapsulation. For example, nanoencapsulation of probiotics ensures that the dietary supplements are well preserved and delivered to target destination in the gastrointestinal tract (de Azeredo 2009). Lipids are similarly preserved until they are efficiently delivered to targeted sites, while some products (such as *"Novasol,"* developed by a German company) are used to introduce other dietary supplements that protect the contents from stomach acids (Joseph and Morrison 2006).

9.3.5 Enhancement of Rheological Properties

Another important application of nanotechnology in food processing is for the improvement of rheological and anti-caking properties in food. Nanoparticles are added to many foods to enhance their ability to flow during processing among other things. For example, alumino-sillicate materials are commonly used to inhibit caking in granular materials such as flour (Ashwood et al. 2007; Powell et al. 2000).

9.3.6 Fortification of Food

Nanotechnology is also employed in the fortification of foods. Dairy products, cereals, breads and beverages are now fortified with minerals, vitamins, probiotics, antioxidants, etc. Some of these are added as nanoparticles of a few hundred nanometers in size (Joseph and Morrison 2006; Pradhan et al. 2015; Shelke 2016). For example *Spray for Life* is a vitamin supplement developed by **Health Plus International** for fortifying beverages with vitamins using nanoencapsulation (Pradhan et al. 2015). *Duty Boost* is another product used by another company known as **Jamba Juice Hawaii** for nanoencapsulation of fortified vitamins or bioactive components in beverages (Pradhan et al. 2015).

9.3.7 Others

Nanoceramic products are now used to drastically reduce oil use in restaurants and fast food establishments (Joseph and Morrison 2006; Jones et al. 2016). The large specific surface of nanoceramics prevents the oxidation and agglomeration of fats in deep fat fryers. It also helps oil to heat up faster resulting in shorter frying time with reduced oil consumption. It thus significantly extends the useful lifespan of the oil and improves the crispiness and taste of the fried food (Jones et al. 2016).

A relatively new research area involves the encapsulation of digestive enzymes within a non-toxic polymer shell. The enzyme-filled nanoshell has been shown in laboratory animals to have the capacity to absorb ethyl alcohol from the bloodstream, thereby giving rise to reduced alcohol levels in the bloodstream. A potential use of this idea is in the treatment of alcoholics. Treatment of hair loss through the process of encapsulation is also another potential application (Liu et al. 2013).

9.4 Food Packaging and Food Safety

The purpose of food packaging is to provide a tamper-proof physical protection against external shock and vibration, microbial infestation, ingress of oxygen and other spoilage-causing fluids, among other things. Good packaging also ensures that the quality of food remains unchanged and that the food is kept safe for consumption over a reasonable period of time. Nutritional information is also provided on food packages.

Nanotechnology is currently widely applied in food packaging; in fact the earliest application of nanotechnology in the food industry is in food packaging. Nanotechnology is applied in the development of high barrier and stronger biodegradable plastics, detection of microorganism and other contaminants in packages, introduction of antimicrobial, scavenging of undesirable flavours and spoilage-causing gasses, minimizing of the loss of desirable gases in packaged food, tracking of contaminants in food in transit, etc (Prasad et al. 2017).

9.4.1 Barrier Protection

Oxygen is perhaps one of the most problematic factors in food packaging as it causes food spoilage and deterioration. A good packaging must provide an inert, low-oxygen environment to ensure the inhibition of microbial growth and so avoid spoilage. It must be impermeable to gas. Nanotechnology is applied in the development of new packaging materials which provides a barrier against the penetration of oxygen and other gases. Some of the packaging materials act as oxygen scavengers thereby improving the barrier properties of the packaging and thus impeding their deterioration (Joseph and Morrison 2006). Others are designed to prevent the escape of CO_2 from carbonated beverages while others are employed to reduce the exposure to packaged foods to ultraviolet radiation (Sorrentino et al. 2007).

Exfoliated nanoclay-polymer composite plastic is an example of a nanocomposite material used for the creation of gas barriers. This plastic provides a longer and more tortuous route through which oxygen has to permeate and so provides a barrier to oxygen penetration and prolongs the shelf life of the packaged product (Weiss 2009). *Aegis* is a commercially available South Korean-made nanomaterial that improves barrier properties of nanoclay-based polymers by scavenging for oxygen and retaining the carbon dioxide in carbonated drinks (Flanagan and Singh 2006; Pradhan et al. 2015). An additive of nano-titanium dioxide in plastic is known to reduce ultraviolet radiation damage of foods in transparent packaging (El Amin 2007; Alfadul and Elneshwy 2010).

9.4.2 Beer Bottling Improvement

Beer is generally shipped in glass bottles or metal cans. These are heavier and more liable to breakage than plastic bottles. Shipping in plastic bottles would obviously be cheaper and lighter but beer reacts with plastics severely shortening the shelf life. Clay-based nanocomposites are now employed in the manufacture of plastic bottles to extend the shelf life of the beer and make the bottle shatter-proof. Embedded nanocrystals in the plastic create a molecular barrier that helps to prevent the ingress of oxygen into the bottle as earlier described. The technology currently keeps beer fresh for 6 months but some researchers and companies such as

Nanocor and **Southern Clay Products** are said to be already working on extending the shelf life to 18 months (Joseph and Morrison 2006; Ravichandran 2010; Silvestre et al. 2011).

9.4.3 Enhanced Mechanical Properties of Biodegradable Plastics

Non-biodegradable plastics contribute greatly to environmental pollution problems by causing changes in the nature of soils and by accumulation of greenhouse gases (GHG) in the atmosphere which leads to global warming. Biodegradable plastics provide a solution to this problem but lack the needed mechanical strength. It is also permeable to water and gases. Nanomaterials made of synthetic nanoparticles are now incorporated in packaging materials resulting in packaging materials that are not only biodegradable and impermeable to moisture but have high mechanical strength. *Durethan*, a commercially available nanomaterial made of polyamide, is used to provide stiffness to paperboard containers for fruit juices (Flanagan and Singh 2006).

9.4.4 Antimicrobial Packaging

Food safety refers to the protection of food from chemical, biological, physical and radiation contamination through processing, packaging, storage and distribution (Alfadul and Elneshwy 2010). A number of antimicrobial packaging materials are employed to control microbial growth, prevent spoilage and ensure food safety. Silver nanoparticles are commonly used for this purpose since they are known to have a wide broad spectrum effects on bacteria and other pathogenic microorganisms (Dingman 2008; Chellaram et al. 2014; Aziz et al. 2014, 2015, 2016). Zinc, titanium and magnesium oxides are other nanomaterials with antimicrobial properties used in coating food packaging and surfaces of kitchen wares, refrigerators, etc. (Ravichandran 2010).

9.4.5 Smart Packaging

Smart packaging is designed to respond to environmental conditions and alert the consumer if the quality of the food is compromised. This it does through devices either incorporated with or attached to the packaging. It is also designed to repair small holes or tears. Potential nanosensors could indicate the temperature, freshness, ripeness and contaminant/pathogen status of the package (Brody et al. 2008; Chaudhry and Castle 2011). They could also detect changes in colour, light and humidity in packaged food or any gas produced during spoilage.

For sensing volatiles, “electronic noses,” which are silicon chips covered by a monolayer of organic material to which the receptors are bonded, are used. These chips are connected to a data processing system. The receptors absorb volatiles (produced by the packaged food during the process of deterioration) which dock on them. The docking process causes a change shift which generates a signal in the silicon chip (Kempers 2009; Pradhan et al. 2015). The sensitivity of the sensors can be improved by using single-walled CNTs and DNA. Conducting polymers are also used especially for making sensors for detecting changes in quantity or composition of gases in packaged foods. Such changes results in change in resonance which in turn gives rise to a response pattern on the polymer-based sensors (Ribeiro et al. 2008; Pradhan et al. 2015).

“Electronic tongues”, which are employed in detecting changes in gas composition of packaged food, use principles similar to electronic noses. The released gases trigger a change in colour when they come in contact with the sensor giving a clear visible signal that alerts the consumer on the state of the food, i.e. whether it has been contaminated or has begun to spoil (Joseph and Morrison 2006; Vidhyalakshmi et al. 2009; Ravichandran 2010; Pradhan et al. 2015). Other sensors contain a light-emitting protein that is designed to bind to surfaces of microbes such as *Salmonella* and *E. coli*. When bound, it emits a visible glow which allows for easy identification of contaminated food or beverages (Joseph and Morrison 2006).

The cantilever technology is another sensing device. It is a small portable device in which the tip of a cantilever is coated with chemicals allowing it to bend and vibrate when it binds specific molecules such as those found on the surface of bacteria (Joseph and Morrison 2006). Portable chemical, pathogens and toxins detection devices circumvent the need to send food samples to laboratories for analyses. The laboratory approach is not only costly but time consuming.

It should be noted that measurement of volatiles is a more accurate method of monitoring and controlling product quality in such process as baking than the use of temperature measurement currently employed (Kempers 2009). Nanosensors also enable early detection and identification of microorganisms and so able to detect how safe a food is for consumption. This principle is currently being used by the US Defence Force for pathogen detection in time of bioterrorism attack on food supplies.

Some packages are designed to release nanoscale antimicrobial, antioxidant nutraceuticals as well as other preservatives into foods and beverages in response to growth of microbial population, humidity or other packaging conditions, thus extending the shelf life and improving the organoleptic properties of the packaged food. Chemical release packages may incorporate continuous monitoring elements where the release of the nano-chemicals will occur in reaction to particular trigger elements. Other packages are equipped with nanosensors designed to track either the internal or external conditions of the food products, pallets and containers such as temperature, humidity and other parameters over time and throughout the supply chain. Based on the motoring, such packaging provides relevant information of these conditions (Alfadul and Elneshwy 2010).

9.4.6 Enhanced Shelf Life for Fruits and Vegetables

Among the causes of deterioration of fruits and vegetables is loss of moisture which results in loss of turgor in vegetables and firmness in fruits. Ripening is also accelerated in some fruits by ethylene gas which is produced in the process of ripening of these fruits. Edible wax nanocoating for fruits which are as thin as 5 nm has been developed and widely used to prevent weight loss and shrinkage in fruits (Alfadul and Elneshwy 2010). These coatings are not detectable by the human eye because of their nano thickness. It can also be used on cheese, meats, confectionary, pastries and fast foods to impede migration of moisture and gases. Other nano-based technologies are used to scavenge for ethylene gas that hastens ripening of stored fruits and vegetables (Sekhon 2014; Nanowerk 2016).

9.4.7 Dirt-Repellent Coatings for Packages

Dirt-repellent coating for packages and other food processing equipment have been developed by coating such surfaces with a nanoscale layer of wax. This coating produces a “lotus effect” on the surface, i.e. a phenomenon in which water forms bead and runs off the surface of lotus leaves as a result of nanoscale wax coating on the leaves. Abattoirs and meat processing plants in particular could benefit from such technology (Joseph and Morrison 2006).

9.4.8 Food Monitoring and Tagging

Nanotechnology is also applied in monitoring and tagging of food items. Radio frequency identification (RFID) technology is now incorporated in food to improve supply chain efficiency (Joseph and Morrison 2006; Anonymous 2016). Although very costly at the moment, the technology is already being tested by some large retailing chains like Wal-Mart, etc. It consists of microprocessors and antenna that can transmit data to a remote wireless receiver eliminating the need for manual scanning and line-of-sight reading and enabling automatic reading of hundreds of tags over a short period of time.

Other nano-based technology for tracking packages in transit includes the nanobarcode which, although developed primarily for anti-counterfeiting purposes, can be used for tracking individual items or pallets (Roberts 2007). This device requires a modified microscope to read it.

9.4.9 Others

Titanium oxide nanoparticle-based inks for sensing oxygen are used in tamper proofing of food packages (El Amin 2006). Nano protective coatings are used to provide heat insulation and corrosion protection of dairy processing equipment. For example, *Nanusulate-PT* developed by **Industrial Nanotech (OTC:INTK)** is used to protect dairy processing tanks and pipes against corrosion and to insulate them against thermal loss, thereby increasing the efficiency and profitability of the manufacturing process by reducing both energy and maintenance costs (Pehanich 2006; Alfadul and Elneshwy 2010).

9.5 Health Hazards and Regulatory Issues

Although nanotechnology has wide applications (both current and potential) in the food industry, some of the nanomaterials are likely to have some health implications. Absorption of food materials and its metabolic activity increases with decrease in particle size (Chawengkijwanich and Hayata 2008; Pradhan et al. 2015). This implies, in case of toxic materials, that the level of toxicity will equally increase as the particles tend towards nano dimension. With the much reduced particle size, nanomaterials are more mobile, more reactive and so likely to be more toxic (Ravichandran 2009). Also for structured nanomaterials such as nanocomposites or nanoemulsions, the rate of digestion and absorption of the component materials into the biosystem may differ, and this is capable of creating some potential health problems (Pradhan et al. 2015).

Another problem which could come as a result of the application of nanotechnology in food processing and packaging is that of bioaccumulation. With the increased bioavailability of nanoscale food additives, bioaccumulation which could prove to be harmful may result. For example, lipids from lipid-based nanoemulsion, which is preferably used for the delivery of components within the biosystem, could lead to cholesterol accumulation with its attendant cardiovascular and obesity problems (Fujishima et al. 2000). Accumulation of silver nanoparticles has been reported to have adverse effects on the human system; it is believed to be geno- and cytotoxic and even carcinogenic (Pradhan et al. 2015). Because of the reduced particle size of nanosilver which enhances their transfer through the epithelial barrier, they could readily form free radicals in the tissues. This could lead to oxidative damage to the cells and tissues (Maness et al. 1999). Some of the nanomaterials such as carbon nanotubes usually migrate into food and can lead to toxic effects on the skin and lungs of human (Mills and Hazafy 2009).

Another area of concern is the impact of disposal of wastes containing nanoparticles on the ecosystem. Migration into and accumulation of disposed nanoparticles in water bodies could prove to be toxic to the flora and fauna of the ecosystem, including planktons. Species that feed on these may also be affected (Pradhan et al. 2015). Migration and accumulation in soils can also result in the disruption of the soil environment. For example, aluminium nanoparticles have been reported to inhibit plant growth (Mills and Hazafy 2009).

Because of all the above potential problems, there is need for regulations to guide the use of nanomaterials and generally the application of nanotechnology in the food industry. Many regulatory bodies are already in place mostly in developed countries. They include the European Food and Safety Authority (EFSA), the

Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) of the USA and the National Institute for Occupational Safety and Health (NIOSH), among others. These agencies are expected to make regulations that govern the use and application of nanotechnology in food. In India and some other developing countries, some form of regulation may be in place but the functionality of such may be in question.

Nanomaterials should be introduced only after these materials have undergone full safety evaluation by the relevant scientific advisory associations or agencies. As enumerated by Pradhan et al. 2015 and other authors, nanomaterials should be free of toxic materials such as heavy metals. They should be free from toxins and mycotoxins. They should not change the inherent taste or odour/aroma of the food. They should be inert and should not have any harmful effects on human health and the environment. They should preserve the quality of the food. If some active component meant for delivery of food supplements is being added to food packaging materials, the materials should first be assessed as a direct food additive (Sondi and Salopek-Sondi 2004; Scampicchio et al. 2008; Alfadul and Elneshwy 2010; Silva et al. 2012; Pradhan et al. 2015). Release of nanomaterials into the ecosystem should be avoided. Generally all nanoparticles incorporated in food should first be properly evaluated for toxic and other negative effects before such incorporation.

9.6 Summary and Conclusions

Nanotechnology has a lot of potential applications in the food industry and is steadily being widely applied in the various facets of the industry. It is applied in processing, preservation, packaging, handling and storage of food. In food processing, nanotechnology is applied to deliver nutrients, increase bioavailability and potency, effect timed and targeted release of nutrients, mask undesirable taste and odours, protect sensitive nutrients, increase solubility and improve rheological and anti-caking properties. It is also applied in the creation of functional, interactive and multicomponent foods and to improve flavour and texture and enhance shelf life of food. In food packaging, handling and storage, it is applied in the development of high barrier and stronger biodegradable plastics, detection of microorganism and other contaminants in packages, introduction of antimicrobial, scavenging of undesirable flavours and spoilage-causing gasses, minimizing of the loss of desirable gases in packaged food, tracking of contaminants in food in transit, etc. Application of nanotechnology in this industry has resulted in enhanced food quality and food safety. Like every new technology involving materials that are ingested or used for packaging ingested products, full scientific assessment needs to be carried out by relevant advisory bodies before they can be fully accepted as safe.

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Impact of the Nanomaterials on Soil Bacterial Biodiversity

10

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Abstract

In this chapter we first review some characteristics of the nanoparticles and nanomaterial. We will explain their definition, main properties, applications, availability, and toxicity to the prokaryotes. Then, we define the soil as a very complex ecosystem and consider some of its physicochemical-biological properties, in order to discuss the action of the nanoparticles and nanomaterials present. We discuss the use of these substances in agriculture and their ecotoxicological effect. We also examine methodologies and techniques currently used for measuring their interaction with microorganisms and microorganism communities and argue that they are indeed potential contaminants. Since their use, especially in agrochemicals, has largely grown in the last years, and there is still not enough data to support the necessary decisions in local and international regulations concerning human health and the environment, it is urgent to develop and extend this kind of studies.

Keywords

Nanoparticles • Toxicity • Ecotoxicology • Soil • Agriculture

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10.1 Nanotechnology

The US Environmental Protection Agency (US EPA 2007) defines *nanotechnology* as the understanding and controlling of matter at dimensions of roughly 1–100 nm, where unique physical properties make novel applications possible (Nowack and Bucheli 2007). This knowledge branch emerged from the physical, chemical, and engineering sciences with the aim of developing new materials, structures, devices, and systems that present properties and functions different from the similar ones at macroscales. A typical example is carbon, a nonmetal that, when forming nanotubes, is one of the best conductors.

According to Santamaria (2012), the first observation and size measurement at a nanoscale was made in 1914 by Richard Adolf Zsigmondy. Thereby, the rise of this science is associated to the development of the scanning tunneling microscope (STM) and the atomic force microscope (AFM), which allowed the manipulation and control of atoms and molecules individually (Prathna et al. 2010; Santamaria 2012). There were exciting news when it was announced that Eigle and Scheweizer could manipulate, in 1989, 35 xenon atoms on a nickel surface to form the IBM logo, initiating the use of applied Nanotechnology.

10.2 Nanomaterials and Their Properties

Nanomaterials (NMs) are materials with morphological characteristics that measured less than 1 µm in at least one dimension. Such materials are usually classified by, beyond their dimensionality, their morphology, composition, uniformity, and agglomeration properties (Nowack and Bucheli 2007). On the other hand, *nanoparticles* (NPs) are substances that have less than 100 nm of size in more than one dimension (Nowack and Bucheli 2007).

The NPs can be divided into natural, incidental, and engineered. The natural ones are ubiquitous in the environment and are produced by natural processes (without human influence); while the incidental are coproduced by processes associated to anthropogenic activities; on the other hand, engineered NPs are produced industrially with specific purposes (Nowack and Bucheli 2007).

The exceptional "abilities" of NPs are associated to the manifestation of quantum effects. When the size of a particle becomes comparable to its fundamental scale (i.e., its wave function), for example, roughly like the Bohr radius for an electron forming an exciton (excited in a lattice), quantum confinement occurs and the energy needed to move an electron (that is, to form the exciton) starts to increase. One of the consequences of it is that, since the energy band gets wider, the wavelength gets shorter, and the ratio of the surface area over the volume becomes larger (Prathna et al. 2010; Dinesh et al. 2012). This can enhance the agglomeration rate, at the same time that the diminution of the particle size leads to more reactivity. Also, the surface charge can facilitate their binding to the targeted biological system (e.g. macromolecules, microorganisms, ions) (Dizaj et al. 2014).

Concerning the NPs' toxicity, there is a clear relation between it and the NP sizes: smaller NPs show a higher toxicity. Due to their small dimensions, they easily enter biological systems and can interact with the macromolecules of the organisms. These interactions can produce ions or free radicals that cause damage to cells, mainly to the DNA itself (Gatoo et al. 2014). Thus, it is important to keep in mind that the physicochemical properties of the NPs depend on a great variety of factors which are strongly influenced by the surrounding environment.

10.3 The Many Applications of Nanoparticles

Different synthesis procedures can manufacture NMs with very particular electronic, optical, physical, and chemical properties (Prathna et al. 2010). These properties, such as size, shape, surface area and charge, crystal structure, chemical composition and reactivity, hydrodynamic diameter, agglomeration, concentration, and porosity and purity, determine their behavior and can be tailored to adjust them for special needs in their targeted application.

Based on quantities in the market, industrial production, and life cycle of NPs, Piccinno et al. (2012) estimate that worldwide NP production is dominated mainly by the ones of TiO_2, ZnO, FeO_x, AlO_x, SiO_2, CeO_2, Ag, quantum dots, carbon nanotubes (CNT), and fullerenes. They found that NMs containing TiO_2 are the largest produced, with approximately 10,000 ton/year, followed by CeO_2, FeO_x, AlO_x, ZnO, and CNT with 100 and 1000 ton/year. According to the literature, NPs are being applied mainly on the areas of engineering, agriculture, electronics, and medicine, particularly on the production of materials for health and fitness, home and garden, electronics and computers, food and beverage, automotive, and appliances (see, e.g., Petersen and Nelson (2010); Santamaria (2012) and Table 10.1). And the commercialized products containing the NMs or NPs are mainly cosmetics, clothing, shoes, detergents, dietary supplements to surface coatings in respirators, water filters, phones, laptops, toys, and commercial home water purification systems (e.g., Nowack et al. 2011; Bondarenko et al. 2013).

10.4 Nanoparticles in the Environment

Undoubtedly, nanotechnology has provided several applications and has driven many innovative developments, becoming important in the global economy (Scott and Chen 2013). However, they may also represent a new source of environmental contamination, not yet controlled or even understood.

NPs released to the environment may come from punctual or non-punctual sources (Table 10.2). Examples of the first sources are production facilities, landfills, and wastewater treatments. While for the second, we can mention the wearing materials containing NPs (Nowack and Bucheli 2007). Also, NPs can be released to natural compartments via sewage treatment plants and waste handling reaching the soil or water bodies, or arrive to them indirectly, for instance, via aerial deposition or

Table 10.1 Use and applications of NPs

Kind of NPs	Applications or potential use	References
Pt, Ag, Au, Cu, Pd, Ni and Rh	Used to modify the semiconductor properties and enhance their photocatalytic activity	Devi and Kavitha (2014)
Fe_3O_4	Drug delivery promise	Guo et al. (2009)
Au and Ag	Candidate to photothermal therapy and promising contrast agent for dark-field image studies	Sau et al. (2010)
MoS_x, Cu, CuO, PbS, TiO_2, ZnS, LaF_3, and WS_2	Lubricant/oil additives	Bakunin et al. (2004), Liu et al. (2004), and Wu et al. (2007)
Cu, CuO, Al_2O_3, TiO_2, and Ni	Used to enhance the heat transfer on fluids, for instance, on solar cells	Ebrahimnia-Bajestan et al. (2011)
CuO and ZnO	NPs' deposition on textiles	Abramova et al. (2013, 2014)
TiO_2	Used as photocatalysts for degrading many organic contaminants	Ohko et al. (2001) and Dasari et al. (2013)
ZnO, TiO_2 and Ag	Used in cosmetics and skin care products	Patel et al. (2011) and Nipane et al. (2012)
Co_3O_4	Used as catalysts, in electrochromic devices, gas sensors, solar energy absorbers, and magnetic materials	Li et al. (2005, 2011), Liang et al. (2011), Zhong et al. (2012), and Dasari et al. (2013)
Al	Potential use as fuels for space launch vehicles, rockets, and missiles	Ohkura et al. (2011) and Ahn et al. (2013)

Table 10.2 Main sources of NPs or NMs released to the environment

NM production	Laboratories or factories can release the NPs during their synthesis processes
Nanoproducts	Released from products containing NMs, such as cleaning products, clothes, detergents, personal care (cosmetics, sunscreens, etc.), technological products (electrodes, conductors, semiconductors, dielectrics), etc.
Intentional discharges	Release of nanopesticides or materials containing NMs, such as municipal wastewater
Transport and storage products	Through the accidental spills, discharges, and leakage

Adapted from Keller et al. (2013)

runoff (Nowack and Bucheli 2007). Nevertheless, previous studies have suggested that the concentration of NPs is higher in soils than in water or air systems; while the soil microbiota and plants are the major eco-receptors of soil NPs (Maurice and Hochella 2008; Klaine et al. 2008; Gottschalk et al. 2009; Tiede et al. 2009).

Concerning the effect of NPs over the biota, in natural compartments, their persistence seems to be an important characteristic, besides their toxicology.

NPs may persist in the system for a long time, be taken by the organisms (possibly bioaccumulated), or even be transferred among organisms of different trophic levels (Anjum et al. 2015).

10.5 Soil

Soil constitutes one of the most fascinating ecological systems, where the microorganisms; micro-, meso-, and macrofauna; microflora; and plant roots interact among themselves and also with the abiotic part, modifying their surroundings although usually on a perfect homeostasis. Following this view, it is appropriate to mention the soil definition proposed by Atlas and Bartha (1986): "The soil is a structured, heterogeneous and discontinuous; fundamental and irreplaceable system; developed from a mixture of organic matter, minerals and nutrients capable of supporting the growth of organisms and microorganisms." It has been recognized that the soil is not an inexhaustible resource and that it may, if inappropriately used or mismanaged, be rapidly lost (Nortcliff 2002). It governs plant productivity of terrestrial ecosystems and is very important for the maintenance of most the biogeochemical cycles (Nannipieri et al. 2003).

The main problems associated to the soil are soil degradation and contamination. *Soil degradation* can be defined as "a process which lowers the current and/or future capacity of the soil to produce goods or services" (Oldeman 1994) and is related to: (a) the displacement of the soil material and (b) the deterioration of the soil in situ. Soil degradation can be caused by erosion and by chemical and/or physical factors. From these, soil degradation caused by the erosion is the most studied process and has been recorded since ancient times, reason for it to be recognized as a classical problem of soil loss. Soil erosion is a complex process that depends on soil chemical properties, ground slope, vegetation coverage, and rainfall amount and intensity (Montgomery 2007), usually associated to the changes in land use, such as demographic pressure, deforestation, and/or agriculture. The physical factors that can cause soil degradation are, for instance, waterloggings, subsidence, soil compaction, crusting, and sealing. Chemical factors that can disturb the soil are the loss of nutrients and organic matter, soil salinization, acidification, and pollution (Oldeman 1994).

Highlighting the *soil contamination* topic, there are a vast list of products and processes that can cause some damage to the soil's health, such as waste accumulation, excessive use of pesticides, excessive manuring, oil spills, deposition of airborne pollutants, such as heavy metals like lead (metal refineries), arsenic, zinc, cadmium (motor vehicle emissions) etc. (Montgomery 2007). The NMs must also be included on this list, since their production and applications have grown extensively in recent times and thus their environmental input as a consequence. However, while other kinds of contaminants can easily be recognized as contaminants, it is difficult to make evident that NMs or NPs are the pollutants. For this reason, NPs' contamination is "a kind of invisible pollution" (Gao et al. 2013; Anjum et al. 2015).

10.6 Interaction of Nanomaterials and Nanoparticles with the Soils

Since the soil is a very complex ecological system, composed by different minerals, organic material, and living beings, the interaction of the NPs with it will strongly depend on the soil's parameters, as well as on the properties of the NPs.

The main properties of the soil, that is, the ones that define its fertility (porosity, hydraulic conductivity,[1] cation exchange capacity,[2] pH, and amount of organic carbon), are also important factors for defining the interaction NPs-soil (Nowack and Bucheli 2007; Ben-Moshe et al. 2013). Moreover, the total soil biota (microbial communities, earthworms, nematodes, protozoa, fungi, arthropods, and plants) can affect strongly this interaction (El-Temsah and Joner 2012; Concha-Guerrero et al. 2014; Servin and White 2016). Particularly, the soil retention capacity may be affected by its ionic strength, pH, zeta potential, and texture (Pachapur et al. 2016), while the aggregation ability of soil particles, transport, and eco-toxicity of NMs in the environment may depend on the soil ionic strength, pH, and surface charge (Joo et al. 2009). On the other hand, NPs' mobility inside the soil (mean free path) is probably the main parameter governing their interaction. This is directly related to their relationship with the water; their ability for aggregation or dispersion, adsorption or desorption, and dissolution or precipitation; as well as with their decomposition rate (Dinesh et al. 2012).

Although there is a consensus about the importance of the above parameters, the interaction of NPs-soil itself and the level of toxicity of the NPs are not well defined and sometimes prone to debate. On the case of the organic matter, for instance, while Ben-Moshe et al. (2013) verified no effect of it over the reactivity of the NPs, Nowack and Bucheli (2007) observed that the organic matter could lead to the formation of aggregates of NPs, favoring their precipitation and, consequently, decreasing their bio-disponibility. On the other hand, other authors have shown that the adsorption of NPs to the soil organic matter may enhance their suspension in aqueous solution, therefore increasing the NPs' mobility (Mansouri et al. 2015; Pachapur et al. 2016). Finally, all these studies agree that the capacity of the NPs for acting as sorbents depends on their surface area, reactivity, and ionic charges, as already pointed out.

Anyway, it is paramount to expand our knowledge about the interaction, toxicology, and degradation mechanisms of NPs in the soil and other ecosystems. Only then will we be able to define politics and make informed decisions about the use, risks, advantages, and consequences of the use of NPs in the soil or general release of them to the environment.

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[1] Capacity of a soil, rock, or plant of letting the percolation of a fluid, usually the water

[2] CTC is the total amount of cations ($Ca^{2+} + Mg^{2+} + K^{+} + H^{+} + Al^{3+}$) retained on the surface of the soil colloids (clays, humic substances, and oxides of Fe and Al).

10.7 Use of Nanoparticles in Agriculture

An agrochemical (or agrichemical) is any chemical substance used in agriculture, even if its use is also extended to non-agronomic applications (home and garden, forestry and industry), with the aim to control seeds, competing herbs, insect pests, and diseases in crops (McDougall and Phillips 2003). Examples of agrochemicals are fertilizers, pesticides, herbicides, fungicides, and feed supplements. Once an agrochemical has been applied, one part of it may be volatilized, while the remaining part will be integrated to the soil. Depending on its chemical and physical characteristics, it will be solubilized in the water soil and can be translocated into the plants; but, the excess will remain and be incorporated into the water ground, becoming a great environmental problem hard to mitigate. Besides the contamination of water resources and residues on food products, there are also the health and social problems associated to their application. Nevertheless, agrochemicals have been extensively used to do different degrees in various countries, under different health and environmental laws.

The interest on using NPs in the agriculture has flourished recently, with innumerable applied research projects developing novel nanoagrochemicals, especially the ones known as "nanopesticides" and "nanofertilizers" (Kah 2015). Nanotechnology is a new science which promises a revolution over the old techniques with the introduction of new materials and products better than those that already exist. Specifically for the agriculture, it may improve the area of "precise farming" (e.g., Table 10.3), which searches the means for maximizing agricultural production outputs while minimizing production input, by also meeting the increased needs of the world's sustainability (Chen and Yada 2011).

However, the use and application of such nanoagrochemicals must be regarded as a particularly critical case in terms of environmental impact since they represent a direct source of NPs to the environment. This caution is reinforced by our lack of knowledge of the risks and consequences of these new NMs into the ecosystems. There is a certain consensus that the data to allow a clearly safe assessment for the use of nanoagrochemicals is still insufficient. This leads some to defend that "the application of nanopesticides should be prohibited until they are proven to be entirely safe," although this is, in some sense, unrealistic because all pesticides are inherently toxic (Kah 2015). Also, the use of NPs and NMs is already a reality, as far as the direct contact of people with products that contain them and their release to the environment (Musee 2011; Raj et al. 2012; Keller et al. 2013). The scientific community has different viewpoints: while some tend to convey a very positive image of the nanotechnology (as usually do the material scientists), others prefer to focus on the risks to the environment and human health associated to the use of the NPs (as usually do the environmental scientists) (Kah 2015; Prasad et al. 2017). This debate is important to support decision-making processes, e.g., for local or international regulations, but also for giving objective information to the population and direct users.

Table 10.3 Possible advantages of nanotechnology for agriculture

Nanotechnology	Description	Advantages
Nanoscale carriers	Carriers to store, protect, deliver, and release the intended payload, in the desired specific amount, for crop production process (improves stability against environmental degradation)	May enable the controlled application of agrochemicals, reducing the total amount applied, avoiding overdoses, and minimizing the waste
Field nanosensors	Field sensing systems to monitor the crop conditions and environmental stresses	Real-time monitoring of crop growth, allowing optimal planning and control ling the level of water, fertilizers, pesticides, herbicides, etc.
Nonintrusive nanocomponents	Characterization tools to study physical, chemical, and biological inter actions between plant cell organelles and disease-causing pathogens	Enables the study of plant disease mechanisms for developing treatment strategies
Nanotechnology gene sequencing	Study of genomes of crop cultivates and genetic engineering	Improves plant resilience against environmental stresses and diseases
Lignocellulosic nanomaterials	Development of new nanoscale cellulosic nanomaterials from crops and trees	New nano-biomaterials for food, packaging, construction, and transportation

Adapted from Chen and Yada (2011)

10.8 Ecotoxicology of Metallic NPs to Prokaryotes

It is well known that the microbial abundance in soils[3] is greater than the abundance of eukaryotic organisms (Torsvik and Øvreås 2002). Another point of common consensus is the importance and integrity of the soil microbial pool for the good health of these ecosystems. Thus, it is preeminent to understand the toxicology of NMs and NPs to these microorganisms. Agrochemicals may contain metals (Dizaj et al. 2014), as well as their counterpart containing NMs (Chen and Yada 2011). In this section, we will focus on the understanding of ecotoxicology of mettalic NPs on prokaryotes of soils.

The starting point is the direct interaction between the NPs and the cellular surface. Since the bacterial membrane is negatively charged, when positively charged NPs, such as NPs of Al_2O_3 and SiO_2, are available, they may be attracted by the cells and the interaction is favored, as was observed by Jiang et al. (2009). The negativity of the membrane is usually generated by carboxyl, amide, phosphate, hydroxyl groups, and carbohydrate-related moieties aggregated to the bacterial cell wall, providing sites for molecular-scale interaction with NPs.

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[3] Estimated to amount 26 Pg in cellular carbon, or about 5–7% of the total mass of prokaryotes in the Earth (Whitman et al. 1998).

The studies focused on the cytotoxicological mechanisms caused by metal NPs have pointed mainly two possibilities: free metal ion toxicity coming from the dissolution of the metals by the NPs and oxidative stress via the generation of *reactive oxygen species* (ROS), both on the surface of NPs (Dizaj et al. 2014). Other mechanisms, such as van der Waals forces and electrostatic, hydrophobic, and receptor-ligand interactions, have also been considered as possible explanations for cell damage caused by NPs.

The oxygen-derived prooxidants, or ROS, are long known to cause biological damage, especially to lipids, DNA, and proteins. They can be classified into two groups of compounds: radicals and nonradicals (Kohen and Nyska 2002). The ones in the *radicals group* contain at least one unpaired valence electron and are capable of independent existence (Rice-Evans 1994; Halliwell and Gutteridge 2015). Examples of them are the nitric oxide radical ($NO^•$), superoxide ion radical ($O_2^{•-}$), hydroxyl radical ($OH^•$), peroxyl ($ROO^•$), and alkoxyl radicals ($RO^•$) and one form of singlet oxygen ($^1O_2$). The occurrence of one unpaired electron results in high reactivity of these species by their affinity to donate or obtain another electron to attain stability. The ones in the *group of nonradicals* are also extremely reactive, even though they are not radicals. Among the compounds produced in high concentrations in living cells that can be considered on this group are the hypochlorous acid (HClO), hydrogen peroxide (H_2O_2), organic peroxides, aldehydes, ozone (O_3), and O_2 (Cao and Prior 1998; Halliwell 1990, 1995).

Studies of the generation of ROS on NP surfaces in model microorganisms (Jiang et al. 2009; El-Temsah and Joner 2012; Dizaj et al. 2014; Wyszogrodzka et al. 2016) have pointed that the bactericidal potential decreases as $OH^• > O_2^- > H_2O_2$ (Maness et al. 1999; Anjum et al. 2015). These studies have shown that ROS can cause deterioration of the membrane architecture, leading to alterations in cell-membrane properties; they also interfere on the activity of metalloenzymes and damage the integrity of DNA. Apparently, ROS formation by metallic NPs is a photoinduced mechanism (Dasari et al. 2013; Wyszogrodzka et al. 2016). Indeed, Wyszogrodzka et al. (2016) state that metal NPs cannot be active in the formation of ROS unless directly illuminated by ultraviolet (UV) light and argue that, when ROS is generated, it is probably a defense mechanism. On the other hand, Jiang et al. (2009) and Dasari et al. (2013) verified the production of free radicals by metal NPs, that is, even under dark conditions.

The general action mechanisms of NPs, that is, their capacity to produce ROS, to link to the membrane components, and to be internalized by the cells, are wide and depend on several factors. Overall, it is related to chemical speciation, stability and aggregation of NPs, and their size, shape, and concentration, besides the surrounding physicochemical characteristics (such as pH, luminosity, etc.). As can be seen in Table 10.4, ZnO and TiO_2 are examples of NPs capable to produce ROS (Dasari et al. 2013; Carré et al. 2014). However, it is already unclear if some other NPs, such as CuO, can do the same. For instance, Dimkpa et al. (2011), Dasari et al. (2013), and Concha-Guerrero et al. (2014) verified that bacteria exposed to different concentrations of CuO NPs presented cellular damage and even cell death. Nevertheless, Dasari et al. (2013) and Concha-Guerrero et al. (2014), who used low concentrations of CuO NPs, did not detect ROS production, while Dimkpa et al. (2011)

Table 10.4 Some studies on the toxicology of NPs by using single-species experiments

Results	Reference
TiO_2 photocatalytic reaction causes the lipid peroxidation reaction; as a result, normal functions associated with an intact membrane, such as respiratory activity, are lost	Maness et al. (1999)
On Gram-negative bacteria, the AgNPs (1–10 nm) attach to the surface of the cell membrane disturbing its basic functions, like permeability and respiration; they penetrate the cell where they can interact with sulfur- and phosphorus-containing compounds (such as DNA); they release Ag^+ with bactericidal power	Morones et al. (2005)
AgNPs may target the bacterial membrane leading to a dissipation of the proton motive force	Lok et al. (2006)
NPs' surface changes play a dominant role on adsorption processes	Nowack and Bucheli (2007)
Antibacterial activity of metallic NPs (Al_2O_3 , SiO_2, and ZnO) was observed, indicating possible production of free radicals under dark conditions	Jiang et al. (2009)
Metallic NPs of Ag and CuO showed bactericidal effect, while ZnO NP caused bacteriostasis (≤1 mg Ag/L and ≈10 mg CuO and ZnO)	Gajjar et al. (2009)
Accumulation of intracellular ROS only when the cells were treated with toxic levels of CuO NPs and Cu ions, respectively 500 mg/L and 2.5 mg/L	Dimkpa et al. (2011)
Nano-sized zero-valent iron (nZVI) at ≥500 $mg.kg^{-1}$ showed negative effects on the soil invertebrates	El-Temsah and Joner (2012)
NPs of TiO_2 (1.7 mg/L) and ZnO (0.05 mg/L) produced ROS inducing damage on the *E. coli* cells, while any ROS production was observed by CuO (0.2 mg/L) and $Co_3\,O_4$ (35.0 mg/L)	Dasari et al. (2013)
CuO NPs (160 mg/L) were observed to cause strong damage (e.g., holes and cavities on the membrane cells and cellular death) on soil native bacteria strains (*Brevibacillus laterosporus* CSS8, *Pantoea ananatis* CSA35, *Chryseobacterium indotheticum* CSA28 strains), probably due the formation of Cu^{2+} ions	Concha-Guerrero et al. (2014)
Some evidence of oxidative stress was observed when *E. coli* strains were exposed to MgO NP (1 mg/mL). The cells exhibited severe membrane damage	Leung et al. (2014)
TiO_2 NPs (0.4 g/L) induced production of ROS on *E.coli* culture modifying the membrane structure (proteins and lipids); the $O_2^{\bullet-}/{}^1O_2$ were the main compounds involved in the lipid peroxidation	Carré et al. (2014)
NPs of metal oxides, specially ZnO, NiO, CoO, CuO, and Cu_2O, and their antibacterial activity have been attributed to the formation of reactive oxygen species (ROS)	Wyszogrodzka et al. (2016)
At low concentrations of ZnO NPs (50–100 mg/L), cellular growth was stimulated; at median concentrations (500–900 mg/L), damage on the membrane cells was observed, mainly holes and cavities on the membrane cells; finally, at concentrations as high as 1000 mg/L, cellular death is observed	not yet published

observed the accumulation of intracellular ROS, but only when the cells were treated with hyper-toxic levels of CuO NPs (500 mg/L).

The ability of the microorganisms to grow on biofilms may also affect the interaction of NPs with them. The biofilms usually act as protective layers and are composed by exopolysaccharides (EPS); however, proteins, nucleic acids, (phospho) lipids, and humic substances have also been found on them (Denkhaus et al. 2007). All these compounds may interact with the NPs, probably by reducing their electrostatic interaction and, thereby, decreasing their availability to interact with the cells. Dimkpa et al. (2011), for instance, verified that the presence of EPS could in fact protect bacterial strains against the action of CuO NPs and Cu ions. Similar results were obtained for Cu-doped[4] NPs and TiO_2 NPs by Wu et al. (2010).

10.9 Evaluation of NPs' Toxicology over Soil Microbial Communities

Most published works on the potential ecotoxicology of NPs are based on experiments that use single species. Also, they usually prove laboratory or type strain representatives of a model group (such as *E. coli*, *Pseudomonas* sp., *Paracoccus* sp., *Bacillus* sp., etc.), with very few works using native strains. The advantages of working with model strains are that they are very adapted to laboratory conditions and their physiology is well known, which makes it easier to analyze and compare the results. On the other hand, native strains do not have these advantages, and, worse, they need to be isolated from the environment and characterized to determine their best growth conditions, before the toxicity assays are carried out. Nevertheless, the use of native microorganisms is much more realistic: native strains behave differently from laboratory ones (growth rate, nutritional requirements, etc.) and may respond in a distinct way to any determined environmental stress. Thus, the results obtained with these strains must be used to validate the assays with model strains.

Moreover, single-species experiments only give a glimpse about the effects of the compounds over the microorganisms. As mentioned before, soil is a very complex biological system, and it is necessary to construct experiments as realistic as possible taking into account all the variables and conditions that occur in the environment. An alternative is the use of soil microcosms. By definition, *soil microcosm* is a "replicable experiment unit containing soil and which allow the observation of the ecosystem structure and function." Thus, it must be sufficiently complex to really reproduce the ecosystem under study; that is, it must be self-perpetuating or, at least, have relatively stable communities (Giesy Jr. and Odum 1980; Tarradellas et al. 1996).

In practice, these conditions are hardly obtained since frequently the drying, sieving, and storing of soils for preparing the microcosms change their physical characteristics, as well as the difficulty to maintain the expected humidity and temperature. In order to alleviate these problems, the American Society for Testing and

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[4] Cu NPs to which specific impurities (called "dopants") were added for giving them desired properties.

Materials (ASTM) described a standard method for a minimum soil microcosm (Van Voris 1988). This includes the use of an intact soil core in a system that lets water and sunlight as input and collects the leakage output. Some improved soil-core microcosms were also suggested, as the one proposed by Checkai et al. (1994). Specifically, they incorporate to the standard microcosm: sampling core retrieving techniques for minimal disturbance and controlling of the environmental parameters of the soil – including soil moisture regime (matric tension, rainwater quality, quantity and rate of application) – and soil temperature.

To evaluate the cytotoxicity of NPs, the most frequently reported measurements are the lethal doses (LD) and the inhibitory concentration doses (IC_{25}, IC_{50}), always accompanied by at least one or two chemical, physical, biochemical, and/or physiological additional tests. To directly inspect the physical damage caused to the membrane cells (cavities, holes, membrane degradation, blebs, cellular collapse, and lysis), electronic microscopy observation is often used. Specifically, to evaluate NPs' toxicity in soil microcosms, there are additional techniques that measure the metabolic response of a system (like the Biolog EcoPlates™) and the changes on the community pattern (Brito et al. 2007). Traditional fingerprint molecular tools, such as denaturing gradient gel electrophoresis (DGGE), terminal restriction fragment length polymorphism (TRFLP), clone libraries, and patterns of neutral lipid fatty acids (NLFAs) and phospholipid fatty acids (PLFAs), are frequently used. Pointing to the future, next-generation high-throughput DNA sequencing techniques (MiSeq and HiSeq) will probably replace previous ones for studying the genetic diversity of environmental samples. The combined use of several methods to evaluate the toxicity, especially in the case of the NPs, which have many possible action mechanisms not completely understood, gives more reliability to the results.

Dasari et al. (2013), for instance, measured the metal ions and ROS production, the concentration of specific enzymes (e.g., glutathione), and the peroxidation of lipids for molecular level evaluation. Carré et al. (2014), in turn, used proteomic assays, verifying that TiO_2 NPs modified the protein pattern of the membrane. By using LD, IC_{25}, and IC_{50} indices, the level of exoenzyme esterases (as soil metabolism indicators), the ROS concentration, the metabolic activity, and the direct observation of the cells by electron microscopy analysis, Concha-Guerrero et al. (2014) and Concha-Guerrero (2015) studied the toxic effect of Cu NPs over soil native bacteria. Their results showed no ROS detection although significant cellular death was present suggesting a strong toxicity to the cells. They attributed this damage to the generation of nitrogen reactive species, a hypothesis that still needs to be verified by molecular approaches, by studying the genes involved in nitrogen cycles or by the expressed protein pattern. Another relatively simple technique is the use of Biolog EcoPlates which make possible to perform a screening of metabolic activity of the sample. By applying this approach, our group is studying the effect of the CuO NPs on native strains isolated from agricultural soil samples (Concha-Guerrero et al. 2014) and on microbial communities using soil microcosms (Concha-Guerrero 2015).

Table 10.5 summarizes some results on NPs' toxicity by using model microcosms. These studies show that the NPs tend to form aggregates on soil. The depth on the soil where the contaminant is found, soil texture, and movement of water and

Table 10.5 Soil toxicology assays using microcosms

Soil system	Probed NP(s)	Observations	Methods	Reference
100 g dw of soil (18% water)	CuO	The total number of soil bacterial communities was reduced significantly (48%); also a drift on the composition of the soil community pattern was observed after 30 days	TRFLP[a] metabolic and enzymatic activities	Concha-Guerrero (2015)
6 g dw of soil (80% water)	TiO_2, $TiSiO_4$, FeCo, Ag	All NPs tended to form large aggregates when in soil suspension; all NPs drifted the soil population	DGGE[b]	Nogueira et al. (2012)
5 g soil-sludge (95:5)	PVP-Ag[c], Ag_2S, Ag^+	Ag, populations of actinomycetes, and Gram-negative and Gram-positive bacteria and fungi were impacted, mainly by PVP-Ag and Ag^+ treatments	NLFAs[d] , PLFAs[e]	Judy et al. (2015)
Dry soil	CuO, Fe_3O_4	CuO NPs affected more strongly the bacterial community than Fe_2O_4 NPs; the NPs affected the microscopic properties of the soil	SMP[f] , FTIR[g] and DGGE[b]	Ben-Moshe et al. (2013)
50 g of soil	Fe_3O_4	The NPs stimulated the soil urease and invertase activities and the growth of some bacterial groups (*Duganella*, *Streptomycetaceae*, or *Nocardioides*), although not their relative abundance in the soil	DGGE[b], clone library, RT/qPCR[h], soil enzyme activities	He et al. (2011)
Soil	CNT (C_{60} – Fullerene)	Induced a drift on the soil bacteria community between 20 and 30%	Biomass, DGGE[b], soil respiration	Tong et al. (2007)
200 g of soil	Functionalized CNT	The FMWCNT[i] caused a low shift on the bacterial community composition	RT/qPCR[h]	Kerfahi et al. (2015)
100 g soil + *Cucumis sativa* and *Zea mays* plants	CuO and ZnO	More toxicity was observed from CuO than from ZnO NPs, reducing the biomass of the plants	Metabolic and enzymatic activities	Kim et al. (2013)

(continued)

Table 10.5 (continued)

Soil system	Probed NP(s)	Observations	Methods	Reference
2 kg of soil + maize seeds	ZnO	The arbuscular mycorrhizal fungi may help to alleviate the ZnO toxic effect in plants; the NPs were accumulated on roots and shoots of maize plants	Root colonization, EM [j], photosynthetic pigments	Wang et al. (2016)
2 kg of soil + soybean seeds	ZnO	Electro-dense ZnO NP deposits in stem and root cells were observed; the ZnO NPs inhibited the elongation and growth of the plant	EM [j], metals	Yoon et al. (2014)
Soil + earthworms	Al_2O_3	The Al_2O_3 NPs can impact on the reproduction and cause earthworm behavior changes (*Eisenia fetida*)	Biomass, metals	Coleman et al. (2010)

[a] *TRFLP* terminal restriction fragment length polymorphism
[b] *DGGE* denaturing gradient gel electrophoresis
[c] *PVP-Ag* polyvinylpyrrolidone coated with AgNP
[d] *NLFAs* neutral lipid fatty acids
[e] *PLFAs* phospholipid fatty acids
[f] *SMP* soil macroscopic properties (porosity, hydraulic, conductivity, amount of organic matter, cation exchange capacity)
[g] *FTIR* Fourier transform infrared spectroscopy
[h] *RT/qPCR* real-time qPCR
[i] *FMWCNT* functionalized and raw multiwalled carbon nanotubes
[j] *EM* electron microscopy analysis

pollutants on it also affected, in different ways, the toxicity of a contaminant (El-Temsah and Joner 2012). The behavior of the exposed biota, such as its home range, also defines its exposition to the xenobiont (El-Temsah and Joner 2012). In almost all of these experiments NPs did modify the structure of the microbial soil communities.

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11 The Impact of Engineered Nanomaterials on Crops and Soil Microorganisms

Shiying He and Youzhi Feng

Abstract

With the increases in the applications of nanocontaining biosolids and agrochemicals to agricultural fields, engineered nanomaterials (ENMs) are inevitably released into soils. This ENM accumulation may pose risks to agricultural ecosystems. Both crops and soil microorganisms are susceptible to ENMs. Recent findings demonstrate that ENMs have detrimental or beneficial effects on crops and soil microbial communities, which could subsequently bring unknown implications in food chain. Thus, there has been an increasing concern about the impact of ENMs on plant and microorganisms alone and/or in combination. This chapter emphatically documented the recent researches on the responses of plant and soil microorganisms and their potential feedback to different ENMs. More importantly, there is mutual relationship between plant and soil microorganisms, forming a plant-microbial ecological system. The future research should be emphasized on the combined roles of plants-microorganisms in the ENM ecological functions, which is vital to the comprehensive evaluation of ENM effects on agroecosystem.

Keywords

Nanomaterials • Plant • Soil microorganisms • Toxicity

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11.1 Introduction

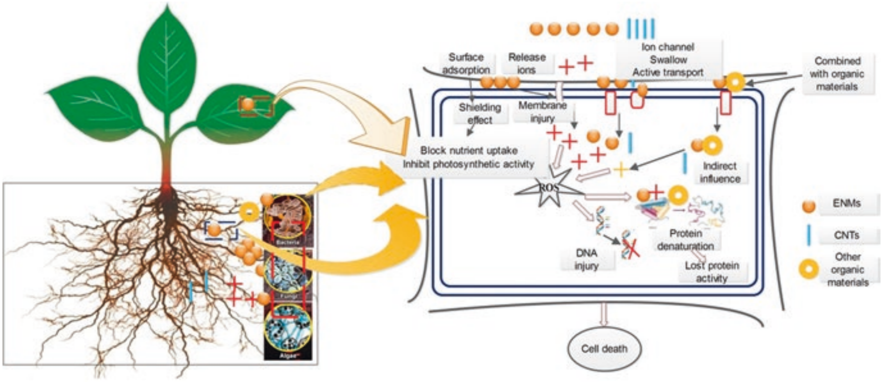
Nanomaterials are the atomic or molecular aggregates with at least one dimension between 1 and 100 nm. Their structures are complex and different from those of large-scale materials. In recent years, nanomaterials have been widely studied, due to their novel properties and functions such as small size effect, surface and boundary effect, enhanced surface-to-volume ratio, and quantum size effect (Nel et al. 2006; Prasad et al. 2016, 2017). These properties are unique and can be tailored to the specific applications leading to a burgeoning nanotechnology industry. With the increasing development of nanotechnology, a great number of engineered nanomaterials (ENMs) have been applied in industry, agriculture, food, commodity, and medicine (Prasad et al. 2014, 2017; Prasad 2014).

According to the different components, ENMs can be generally grouped into four types: (1) carbon-based materials such as carbon nanotubes and fullerenes; (2) metal-based materials such as Au, Ag, metal oxides and quantum dots like TiO_2, ZnO and Fe_2O_3; (3) dendrimers or nanosized polymers; and (4) composites combining nanoparticles with other nanoparticles and/or larger bulk-type materials. It is reported that the ENM yield was 1300 t annually and expected to reach 5800 t annually around 2020 (Klaine et al. 2008). As production and use of ENMs rise, they are increasingly entering and will continuously enter a wide variety of environments including air, water, sediment, and soil during their manufacture and use, which leads to the potential ecological effect (Brayner et al. 2006). Recently, a lot of interdiscipline scientists have reported the toxic-ecological effects of ENMs (Ma et al. 2010; Qiu 2012), among which most are focused on aquatic environment and pure cultivation-simple medium (Klaine et al. 2008). However, their effects on soil ecosystem are still scarce. Soil is deemed as the final pool of different pollutants, and it plays an important part in forming human civilization as it is the matrix of crop cultivation. Thus, the knowledge of influence of ENMs on soil ecosystem, especially agricultural ecosystem, needs paying more attention.

The exposure pathways for ENM exposure to plants and soil microorganisms are through the application of biosolids to agricultural lands and nano-enabled agricultural products including pesticides, fertilizers, plant protector, soil additives, and growth regulators and the application of soil remediation nanotechnologies. It is estimated that the amount of ENMs in biosolids is in the range of 10^{-6}–10^{4} ppm depending on types of ENMs (Gottschalk et al. 2009). ZnONPs, chitosan NPs, carbon nanotubes, or nanoporous materials have been used as fertilizer in agriculture which would potentially lead to the ENM accumulation in soil through time from the repeated inputs. Fe and FeONPs have been used for soil remediation of organic and inorganic pollutants. This exposure pathway may be more serious in specific locations such as polluted soil or place nearby the sewage treatment. Furthermore, the ENMs can migrate from air and water into soil through atmospheric deposition, rainfall, and irrigation. Thus, the concentrations of ENMs are actually much higher in soil than in air and water as expected previously due to their weak transfer ability. For example, Gottschalk et al. (2009) found that the concentrations of TiO_2, ZnO, Ag nanoparticles, and carbon nanotubes in soil are approximately 6.36 μg kg^{-1}, 0.6 μg kg^{-1}, 99.6 μg kg^{-1}, and 6.72 μg kg^{-1}, while 0.002 μg L^{-1}, 0.001 μg L^{-1}, 0.116 μg L^{-1}, and 0.001 μg L^{-1} in water and 0.0005 μg m^{-3}, 0.005 μg m^{-3}, 0.002 μg m^{-3}, and 0.001 μg m^{-3} in air, respectively. Subsequently, the ENMs accumulated in soil may pose risks to agricultural ecosystems. Concerns have therefore been raised over their potential risk on agricultural ecosystem health. The consensus for now is that ENMs can enter biological cells, release metal ions, generate reactive oxygen species (ROS), and absorb organic materials in soil. Thus, these processes will directly and indirectly affect plants and soil microorganisms. Recently, there has been an increasing concern about the impact of ENMs on plant and microorganisms alone and/or in combination. Some data on the responses of plant and microorganisms to ENM exposure have been obtained. For example, ENMs showed different effects on the germination and/or root growth of some plant species. Soil microorganisms are pivotal in maintaining the health and services of terrestrial ecosystems. Cu, Ag, ZnO, Fe, and TiO_2 showed various effects on soil microorganisms. Most of the studies are based on plants or microorganisms alone. In fact, there is mutual relationship between plant and soil microorganisms, formatting a plant-microbial ecological environment. Thus, the effect of ENMs on plant varied with the microorganisms' participation (Dimkpa et al. 2015; Feng et al. 2013). This chapter emphatically introduced the recent researches on the responses of plant and soil microorganisms and their feedback to different ENMs.

11.2 The Mechanisms of ENMs' Biological Toxicity

As shown in Scheme 11.1, ENMs may affect plant and microorganisms at cell, protein, and gene level. While toxicity mechanisms have not yet been completely elucidated for most ENMs, possible mechanisms include disruption of membranes or membrane potential, oxidation of proteins, genotoxicity, interruption of energy transduction, formation of reactive oxygen species (ROS), and release of toxic constituents (Keller et al. 2010). Due to their specific own nature, the biological toxicity



Scheme 11.1 Mechanisms of ENMs affecting plant/soil microorganism ecosystems

of ENMs may occur through the following means: (1) ENMs can absorb and enter organisms, destroying the cell integrity, and may interact with the cellular macromolecules. Most cells of plants, algae, and fungi possess cell walls that constitute the primary sites for the entrance of ENMs. The diameter of pores across the cell wall ranges from 5 to 20 nm. The small size of nanoparticles (<10 nm) readily enter cells through penetrating the cell membrane, nuclear membrane, and ion channel. Larger size of nanoparticles (>10 nm) enter cells through swallow, active transport or destroy cell membrane integrity. As soon as the ENMs enter the cell, they may bind with different types of organelles and interfere with the metabolic processes. For example, the adsorption and membranes-internalization of FeONPs outside and inside bacterial cells were identified, which led to the bacterial genomic mutations (He et al. 2011a). FeONPs were also found to uptake and transport by pumpkin grown in solution culture (Zhu et al. 2008). ZnONPs passed through the epidermis and cortex of roots of *Lolium perenne L.* (ryegrass). (2) ENMs can adhere to the cell membrane adsorption and electrostatic force, subsequently alter the structures of cell membrane, produce shielding effect, etc. For example, it was investigated by microscope that Ag NPs were adsorbed to the plant root surface and pass through cell membrane and then transported to other tissues, affecting the plant growth (Yin et al. 2011). ENMs adhere to plant cell surface, and subsequently their shielding effect can inhibit the plant photosynthesis (Navarro et al. 2008). TiO_2 and ZnONPs induced modifications in photosynthetic activity, biochemical composition, and anti-oxidative enzyme activity in cucumber, green peas, and lettuce. Meanwhile, the adhesion of ENMs will plug in the ion channels, disturbing nutrient transport and ion exchange (Pramanik et al. 2008). (3) Some results indicate that the stress-induced ROS could be a critical factor resulting in cell oxidative damage, lecithin membrane peroxidation, mitochondria damage, protein denaturation, DNA damage, etc. (Chakraborti et al. 1999). ROS can be formed via radicals, transition metals, or other chemicals on the particle surface or as a consequence of the interaction between particles and cellular components. Oxidative stress has been reported in the tissues of aquatic organisms during ENM exposure. ZnO and TiO_2NPs are capable of generate ROS, and the damaging effects of TiO_2NPs on bacteria have been shown to be enhanced by sunlight. Other ENMs, such as AgNPs and fullerenes, also showed the capacity to produce ROS upon UV exposure. Studies on the antibacterial activity by aqueous suspensions of fullerenes suggested that the degree of toxicity to *E. coli* was linked to production of ROS. (4) The release of metal ions by ENMs was proved to have impact on biological organisms: CuO and ZnO NPs were found to release Cu and Zn ions, respectively, which is attributed to the oxidative stress and inhibition of plant growth (Dimkpa et al. 2012). Nanoparticles of Ag and Au manifested dissolution by as much as 17 and 8.0%, respectively, after 28-day amendment in soil. Both Ag and CuONPs have been shown to dissolve in a sand matrix. (5) Due to the high specific surface area and adsorption ability, ENMs can absorb pollutants (heavy metal, pesticide, etc.) and change the latter bioavailability, which is synergistically affecting plants. Trace-metal ion speciation might be altered by ENMs, therefore altering their bioavailability and potential toxicity. Organic pollutants may be interacted with hydrophobic ENMs such as CNTs and fullerenes.

The presence of TiO_2NPs has been shown to increase the accumulation of cadmium and of arsenate in carps because of their strong sorption capacity for these elements (Zhang et al. 2007). *E. coli* exposure to 100 mg/L of bare Fe^0NPs resulted in a 2.2-log inactivation after 10 min and a 5.2-log inactivation after 60 min. Adsorbed poly (styrene sulfonate) (PSS), poly (aspartate) (PAP), or natural organic matter (NOM) on Fe^0NPs significantly decreased its toxicity, causing less than 0.2-log inactivation after 60 min(Li et al. 2010). The decreased toxicity in the presence of NOM or adsorbed polyelectrolyte is that the electrostatic repulsions afforded by the adsorbed polyelectrolyte are limiting adhesion to the bacteria. It was also found that the addition of salts enhances the aggregation of ZnONPs and consequently affects the dissolution behavior and biological availability of the particles (Stewart et al. 2015). Also, the inhibition of bacterial viability counts by AgNP exposure was found to be less in the presence of humic acid (HA) due to its adsorption/binding of Ag NPs (VandeVoort et al. 2014).

In general, the mechanisms of ENM toxicity are complicated and still not illustrated for now. Their physiological toxicity contains various aspects, not just the abovementioned. Further investigations should be definitely carried out to figure out the explicit and comprehensive mechanisms of toxicity of ENMs, in both short- and long term.

11.3 Effects of ENMs on Crops

11.3.1 The Summary of the Effects of ENMs on Plants

Plants are the important and dispensable part of terrestrial ecosystem and play critical roles in the fate and transport of nanoparticles throughout the environment via uptake and bioaccumulation. Thus, their responses to ENMs are fundamental to reveal the ENM ecological effects. Several reviews have already extensively examined the implications of ENM absorption, translocation, accumulation, and biotransformation in food crops and have found some strong evidences that ENMs can yield both beneficial and adverse effects in plant systems at the physiological, biochemical, and genetic levels. According to the statistics announced by Woodrow Wilson Center (Scholars 2009), the effects of most commonly used ENMs (Ag, ZnO, TiO_2, FeONPs, and CNTs) on plants in various cultivated mediums are shown in Table 11.1.

ENMs show the promotion, inhibition, and no significant influences on plants. The specific effect mainly varies by the characters of ENMs and species of plants: (1) Different ENMs showed various effects on plants. There are several examples. Positively, CNTs can promote the root growth of onion and cucumber (Canas et al. 2008). FeONPs can stimulate the growth of mung bean (*Vigna radiata*) by increasing its physiological activities (Ren et al. 2011). Fullerene exposure triggered abnormal cell division in *Arabidopsis thaliana* roots via the disruption of auxin signaling. Furthermore, some metal EMNPs (e.g., TiO_2 and Al_2O_3) are found to enhance the elongation of roots in cucumber and *A. thaliana*. Negatively, AgNPs

Table 11.1 Influences of ENMs on plants

ENMs	Particle size (nm)	Concentration (ppm)	Plant	Growth media	Observed effects	References
Ag	100	500, 1000	Cucumber	Hydroponics	Inhibit root growth, reduce transpiration rate and biomass	Stampoulis et al. (2009)
	<100	100	Onion	Hydroponics	Destroy cell membrane, reduce cell division	Kumari et al. (2009)
	10	0.5, 1.5, 2.5, 3.5, 5.0	Wheat	Sand	Inhibit root growth, show dose effect	Dimkpa et al. (2013)
	5, 20	20, 40, 60, 80, 100	Flax, Ryegrass, Barley	Soil	No obvious effect	El-Temsah and Joner (2012)
	10	100, 1000	Tomato	Hydroponics	Reduce biomass and chlorophyll content, Ag accumulated in tomato	Gardea-Torresdey et al. (2012)
	20	20, 40, 60	Borage	Soil	Inhibit ethylene action, no obvious effect on chlorophyll	Seif et al. (2011)
FeO	20	500	Pumpkin	Hydroponics	NPs enter organisms, but show no obvious effect	Zhu et al. (2008)
	7	62, 100, 116	Cucumber, lettuce	Hydroponics	No obvious effect	Barrena et al. (2009)
	10	250, 500, 750	Soybean	soil	Increase leaf and pod dry weight	
TiO_2	5	2500	Spinach	hydroponics	Promote the photosynthesis	Yang et al. (2007)

	40	91	Wheat	Soil	Reduce biomass, NPs adsorbed on cell walls	Du et al. (2011)
	27	50 ~ 4000	Cucumber	Hydroponics	Promote P,K nutrient uptake, root growth, and chlorophyll content	Servin et al. (2012)
	27	50, 100, 1000, 2500, 5000	Tomato	Hydroponics	Enhance superoxide dismutase activity	Song et al. (2013)
Functionalized carbon nanotubes		9, 56, 315, 1750	Tomato, cucumber, onion, lettuce, cabbage, carrot	Hydroponics	Inhibit lettuce, cucumber, onion root growth, NPs accumulated at root surface, but not adsorbed by plant	Canas et al. (2008)
Nonfunctionalized carbon nanotubes		56, 315, 1750	Tomato, cucumber, onion, lettuce, cabbage, carrot	Hydroponics	Inhibit lettuce root growth, NPs accumulated at root surface, but not adsorbed by plant	Canas et al. (2008)
Multiwalled carbon nanotubes (MCNTs)		50, 200	Tomato	Soil	Improve plant height and flowers, CNTs enter plant organism especially in flowers	Khodakovskaya et al. (2013)
Cu	50	1000	Cucumber	Hydroponics	Reduce biomass, inhibit root growth	Stampoulis et al. (2009)
		0.013%	Lettuce	Hydroponics	Increase root-shoot ratio	Shah and Belozerova (2009)

(continued)

Table 11.1 (continued)

ENMs	Particle size (nm)	Concentration (ppm)	Plant	Growth media	Observed effects	References
ZnO	5	45	Wheat	Soil	Reduce biomass, release Zn^{2+}, and enter plant organisms	Du et al. (2011)
	8	500, 4000	Soybean	Hydroponics	Promote(500), or inhibit (4000) plant growth	Lopez-Moreno et al. (2010)
CeO_2	19	1000	Ryegrass	Hydroponics	NPs enter organisms, inhibit seedling growth	Lin and Xing (2008)
	10	100, 500, 1000	Soybean	Soil	Inhibit plant growth, affect the belowground biomass and function, and shut down the nitrogen fixation	Priester et al. (2012)
Fullerol	20	0.0001, 0.005, 0.0115, 0.05	Bitter melon	Soil	Increase the biomass, fruit length, weight and yield	Kole et al. (2013)

inhibit the root growth of onion and cucumber through destroying cell membrane and root system (Gardea-Torresdey et al. 2012). CuONPs inhibit seedling growth of mung bean and wheat. CuONPs are more toxic to wheat than ZnONPs correlating with the differential phytotoxicity of Cu and Zn ions. (2) Even same kind of ENMs has different effects on different plants. CNTs promote root growth of onion and pumpkin, while have no obvious influence on cabbage and carrot, and even inhibit root growth of tomato (Canas et al. 2008). ZnONPs reduced the biomass of wheat but improved peanut biomass (Lee et al. 2008). Whereas, ZnONPs does not affect plant growth and gas exchange and chlorophyll content in cucumber. (3) Dosage effect exists in ENM-plant effects (Rico et al. 2011). The high concentration of FeONPs releases iron ions and affects photosynthesis through oxidative stress on plant leaves, leading to the decrease of metabolisms to greater extent (Rãcuciu and Creangã 2009). AgNPs (10 nm) reduce the length of shoots and roots of wheat (*Triticum aestivum* L.) in a dose-dependent manner. When exposed to 40 mg/L AgNPs, seedlings of *Lolium multiflorum* failed to develop root hairs and exhibited highly vacuolated and collapsed cortical cells as well as a broken epidermis and root cap. However, the toxicity of ENMs and dosage is complicated. Their toxicity is due to their surface area. Meantime, ENMs easily aggregate to large particles at the high dosage, leading to the decreased bioavailability and toxicity. So the relationship between the ENM toxicity and dosage is not always linear correlation (Bernhardt et al. 2010). (4) Different surface characteristics and sizes of ENMs result in various effects on plants. Nonfunctional CNTs inhibited growth of tomato, onion, and cucumber, whereas functional CNTs just inhibit growth of lettuce (Canas et al. 2008). AgNPs decreased root biomass and length of ryegrass, and the particles smaller than 6 nm showed larger decrease than particles at 25 nm, which is a strong evidence supporting the theory that the surface area plays a large role in the toxicity of AgNPs on plant (Yin et al. 2011). (5) ENMs in different mediums are of various effects. It was found that AgNPs in soils showed no obvious effect on ryegrass at the concentrations of 20–100 mg kg^{-1}, whereas inhibited root growth and decreased biomass in hydroponics (El-Temsah and Joner 2012). ZnONPs were not detected in the plant tissues in sandy medium but were detected on root surface in nutrient solution.

11.3.2 The Character of Bio-effects of ENMs

The current data about the bio-effects of ENMs on plants include the following aspects: (1) the majority of results were focused on the seedling stage of plants. Due to their small size, ENMs can enter the plant organisms, transfer to aboveground parts from root, and accumulate in the fruit. Therefore, they have certain influence on other organisms or even human health through the food chain (Zhu et al. 2008). It has been identified by the infrared Fourier transform spectrometry (FTIR) that TiO_2 NPs (250–750 mg kg^{-1}) decrease nutritive value of cucumber by changing the chemical properties of fruit such as lipid, amino compound and carbohydrate (Servin et al. 2012). It is urgent to further investigate the ENM effects on plant at different growing stages. (2) The effects of ENMs are always compared with their corresponding ion species. In fact, the characteristics of nanoparticles play a bigger role. For example, it was investigated that there are more inhibition effects of AgNPs on plants than Ag^+. (3) The plant medium is also an important aspect to evaluate the influence of ENMs. FeONPs were accumulated in pumpkin in hydroponics soils, whereas not adsorbed in soil (Zhu et al. 2008). (4) In fact, as diverse ENMs coexist in environment, the co-effects should be focused. For example, CuONPs inhibit the growth of soybean root and aboveground parts, whereas the inhibition effect is reduced in the mixture of CuO and ZnONPs.

11.3.3 The Effect of ENMs on Crop Yields

ENMs alter the physiologies of plants (growth, biomass production, number of leaves, and chlorophyll content), which can directly influence their yield. FeONPs improve the leaf and pod dry weight of soybean, which results in 48% higher grain yield than the control. Moreover, CeO_2NP exposure increases the fruit weight of tomato by 10%. However, ZnO and CeO_2NPs have no obvious effects on the yield of soybean and causes reductions in plant biomass without significant effect on grain production in wheat. At the concentration of 500 ppm, ZnO NPs completely halt grain production. CeO_2NPs do not impact plant growth but cause remarkable reduction in fruit yield at the concentration of 800 ppm. TiO_2NPs do not affect biomass yield in wheat and beans in hydroponic culture, nor tomato fruit production in soil. MWCNTs increase by twofold the flowers and fruits in tomato, whereas fullerol enhances the length, number, weight, and yield of bitter melon fruit by 20, 59, 70, and 128%, respectively.

In summary, most of these studies are conducted at the germination phase or early growth stages and under short exposure times. The literatures are restricted to studies involving the complete plant life cycle. And there is the limited study on the long-term evaluations of ENMs to plant systems. The more study is needed to comprehensively understand the effect of ENMs on whole growth periods of crops, especially in the long-term process.

11.3.4 The Effect of ENMs on Soil Microorganisms

Soil is a unique medium that contains the diverse microbial communities including eukaryotic and prokaryotic microorganisms. Soil microorganisms are pivotal in maintaining the health and services of terrestrial ecosystems. They are the drivers of global biogeochemical cycles such as cycling of carbon, nitrogen, sulfur, and phosphorus. For example, the *Azotobacter* drives soil nitrogen fixation rate; P- and K-solubilizing bacteria boost uptake of essential elements by plants through solubilizing P from organic debris and releasing K from silicate in soil. Because soil microorganisms are especially sensitive to environmental changes, they respond to exotic ENMs. Table 11.2 illustrated some data about the effects of ENMs on

Table 11.2 Influences of ENMs on soil microorganisms

ENMs	Particle size (nm)	Concentration (ppm)	Microorganisms	Growth media	Observed effects	References
Cu	11 ~ 55	1000	*Phytophthora infestans*	Culture medium	Inhibit *Phytophthora infestans* growth	Giannousi et al. (2013)
Ag	20	0.1, 1.0	Arbuscular mycorrhizal fungi	Sand	Promote AMF infection rate	Feng et al. (2013)
		100	Bacillus, *Pseudomonas fluorescens*	Culture medium	Inhibiting effect	Dhas et al. (2013)
	10	30	Malignant pseudomonas	Culture medium	Inhibiting effect, affect metabolism	Gajjar et al. (2009a)
ZnO		100	Bacillus, *Pseudomonas fluorescens*	Culture medium	Inhibiting effect	Dhas et al. (2013)
	70	3, 6, 12	*Botrytis cinerea*	Culture medium	Alleviate Botrytis of grape, apple, and peer	He et al. (2012)
	50	1.0	Pseudomonas	Culture medium	Inhibiting effect, affect metabolism	Gajjar et al. (2009a)
Fe	10	3.2	Arbuscular mycorrhizal fungi	Sand	Inhibit AMF ecological function	Feng et al. (2013)
TiO_2	50	1000	Pseudomonas	Culture medium	Inhibit bacteria growth	Karunakaran et al. (2013)
				Soil	Promote bacteria growth	

microorganisms. These results were based on the responses of plant pathogenic bacteria or probiotics, cultured in pure or sand medium. The investigations in soil medium are limited due to the complex ecosystem of soil. Once in soils, ENMs will interact with abundant organic ligands, including natural organic matter (NOM), which can result in the formation of a coating on the ENMs, changing their aggregation, sorption, and biological activity.

The effects of ENMs on microorganisms from pure culture to soil medium are summarized below: (1) Various ENMs show different effects on microorganisms including inhibition, promotion, and no obvious effect. For example, AgNPs are highly toxic to bacteria, such as *E. coli* and *Staphylococcus aureus* (Ren et al. 2011). Plant growth-promoting rhizobacteria (PGPR) like *P. aeruginosa*, *P. putida*, *P. fluorescens*, and *B. subtilis*, soil N cycle bacteria, nitrifying bacteria, and denitrifying bacteria have been shown varying degrees of inhibition when exposed to ENMs in pure culture conditions or aqueous suspensions. MWCNTs perform toxic effect on soil microorganisms, by decreasing their biomass and altering their community composition. Carbon (fullerenes) NPs have little impact on the structure and function of the soil microbial community composition (Johansen et al. 2008). Nano-TiO_2 and ZnO have negative effects on soil microbial communities and inhibited the soil enzyme activities of protease, catalase, and peroxidase (Ge et al. 2011). FeONPs increased soil bacterial community and facilitate C and N cycling in soil (He et al. 2011b). (2) The microbial toxicity of ENMs has the dose effect. The toxicity of AgNPs is in positive correlation with the concentration (Hansch and Emmerling 2010). When AgNPs are added to soils in amounts ranging from 0.003 to 100 mg kg^{-1} dry weight, only less than 20% of the activity of soil denitrifying bacteria remain at the highest Ag concentration. CuO and ZnONPs resulted in dose-dependent and rapid changes in light output to the root-colonizing bacterium, *Pseudomonas putida* KT2440 (Gajjar et al. 2009b). (3) Even same kind of ENMs has different effects on different microorganisms. The primary types of bacteria are gram-negative and gram-positive bacteria, which differ according to their cell walls. For example, the gram-positive bacteria species *Bacillus subtilis* has been found to be more sensitive to AgNPs than other gram-negative species. In a study of fullerene toxicity, *Bacillus subtilis* was found to be less susceptible than other gram-negative and gram-positive species. Moreover, MWCNTs increase the abundances of *Bacteroidetes* and *Firmicutes*, whereas the abundances *Proteobacteria* and *Verrucomicrobia* are decreased (Khodakovskaya et al. 2013). CNTs have also been found to inactivate *E. coli*, *Staphylococcus epidermis*, but be benefit to soil microbes like *P. aeruginosa* and *B. subtilis.*

In summary, most existing references about the microbial toxicity of ENMs are focused on the microbial community through laboratory culture. Thus, it is needed for experiments that generate exclusive data on the effects of ENPs on microbial community in field conditions or experimental conditions that exactly simulate the natural soil environment. Data are required on the long-term effects of ENPs on soil microbial populations in a range of the soils with varying physical-chemical characteristics and the soils from different ecosystems. There are several factors when studying the effect of ENMs on soil microbial communities: the morphological characteristics and size of the ENMs, their chemical and catalytic properties, speciation in intracellular sites, pathways of transport into bacterial cells, and the specific enzymes that assimilate or detoxify the metals or expel them from cells. Moreover, further investigations should be conducted to supply the information on soil functional microorganisms and reveal the effects of ENMs on soil fungi and the composite effects of multiple ENMs in soil medium.

11.4 Responses of Plant-Microorganisms to Ecological Effects of ENMs

Plant and microorganisms are essential parts of ecology with close relationship and interaction between each other. Plants, as producer of ecology, can secrete saccharides, amino acids, and vitamins by root system, providing energy for soil microorganisms, simultaneously affecting species, abundances, and distributions of soil microorganisms (Kiers et al. 2011). In return, soil microorganisms are decomposer of ecology system and can transform soil organic materials to inorganic nutrient, supplying for plants uptake. Microorganisms also affect pollutions in soil in a variety of ways, for example, they can alter the activity of metals through adsorption, oxide reduction, and metabolism, thus, changing the metal toxicity on plants. ENMs are a new type of potential contaminants in soil. Microorganisms can affect the effects of ENMs on plants by changing ENM biological activity, and the responses of plants also affect ENM impact on microorganisms accordingly.

The plant-microorganism ecological feedbacks to ENMs include two aspects: the responses of microorganisms to ENMs and their effects on the ENM-plant interactions and the feedbacks of plants to ENMs also influence the microbial responses to ENMs. Soil microorganisms are active colloids in soil with a high specific surface area and metabolism activity. They can affect activity of ENMs by themselves or their metabolites and subsequently alter ENM effects on plants. For example, TiO_2NPs alter the polysaccharide composition of cell walls in nodules, delaying nodule formation and nitrogen fixation in garden peas. It is found that *Azotobacter*(*Pseudomonas chlororaphis* O6,PcO6) alleviated the inhibition of CuONPs on soybean (Ha et al. 2010). The decreased toxic effects on plant may be attributed to the factors below: extracellular polymeric substances secreted by PcO6 combining with Cu^{2+} ions released by CuONPs or inducing the aggregation of ENMs. *Arbuscular mycorrhizal fungi* (AMF) were also found to influence the ENM ecological effects. AMF are ubiquitous soil microorganisms that are symbiotic with root over 90% land plants. It was found that the hyphal of AMF showed strong adsorption ability of heavy metals. AMF alleviates the AgNP stress on plant by their infection with plants (Feng et al. 2013). It was observed that the infection rate is increased under AgNP addition, and the NPs are adsorbed to the external hyphae and decreased their accumulation in plant tissues, which decreases the inhibition of AgNPs. AMF alleviates the ZnONP toxic effects on plant by f fixing the Zn in root and or internal hyphae. AMF also helps plants absorb more nutrients. The nutrients (nitrogen, phosphorus, and potassium) uptake of corns is promoted with the assist of AMF. Furthermore, soil microorganisms can regulate plants in contaminated soil. For example, AMF affect the ENM ecotoxicity through molecular regulation of host plants. The results indicated that AMF altered the expression of Zn^{2+} ion transporters MtZIP2 gene on the plant cell membrane and then decreases the metals uptake, alleviating the metals damage to plants (Burleigh et al. 2003). This information indicates that the microbial molecular control on plant could influence the ENM-plant biological effects. Thus, it is important to further study the mechanisms of microbial molecular modulation on plants which would contribute to reveal the mechanisms of microbial functions in changing plant biological responses to ENMs.

Plants not only absorb nutrients from soil but also release various substances such as organic acids, proteins, amino acids, carbohydrates, etc. It was found that there are complicated underground exchanging relations between plant roots and microorganisms (Kiers et al. 2011), and the root exudates affected the microbial response to ENMs. For example, the root secretes of wheat decrease the CuO and

ZnONP toxic effects on *Pseudomonas putida* (Martineau et al. 2014). The relief could be attributed to the coating of root exudates on surface of CuO and ZnONPs, which reduces the biological activity of NPs and affects their ecological effects indirectly. The root exudates of soybean can fix the ZnONPs or dilute Zn^{2+} release and subsequently alter the bioavailability of NPs, alleviating the effects on soil bacterial community (Ge et al. 2014). Thus, the information of plant-ENM-microorganism relationship has a great significance to recognize the ecological effects of ENMs, in which root exudates is the key point.

In summary, the plant-microbial interactions can alter ENM biological activity and produce complicated responses to the ENM ecological effects. The knowledge about this aspect is scarce; the research should be emphasized on the combined roles of plants-microorganisms in the ENM ecological functions, which is vital to the comprehensive evaluation of ENM effects on soil ecosystem.

11.5 Conclusions and Prospects

With the development of nanotechnology and popularity of nanoproducts, there is a potential risk to ecosystem. Especially crops and soil microorganisms are susceptible to ENM contamination through material accumulation in soil from continuous biosolid amendment and the application of nanotechnology in agriculture field. A number of publications have been reported to understand the effects of ENMs on crops and microorganisms. However, current researches only focused a single factor or a simple system, for example, most results on plants are based on hydroponic/sandy medium, and the information in soil system remains elusive. As to microorganisms, most data were mainly derived from pure culture or simple soil matrix lack of plant participation. In fact the characters of soils also generate feedback to ENM eco-effect. For example, AgNPs are adsorbed onto the clay in soil which induced their biological toxicity (Wijnhoven et al. 2009). ZnONPs showed more inhibition of wheat growth in acid soil, whereas the less toxic effect was in alkaline soil (Watson et al. 2015). Thus, it is important to comprehensive evaluate the ENMs' effects on plant-microorganism-soil as a whole.

Therefore, the impact of ENMs on crop growth, soil microorganism community and function, and the mechanisms involved should be further focused. Important questions that need to be resolved by further study are noted below: (1) prediction of the quantity, migration, and fate of ENM in agricultural soils and (2) direct observation on the adsorption, transport, and accumulation of ENMs in plant and microorganisms by using mark and image tracer technology. For example, SiO_2NPs are found to be embedded in the membrane using fluorescence-labeled method (Klaine et al. 2008). In addition, the process of ENM entry into cells is clearly observed using energy filter-type transmission electron microscopy and X-ray tomography (Rorter et al. 2007). (3) Various molecular biological methods should be applied to investigate the mechanisms of ecological effects. (4) Most of current studies are based on pot culture. The studies of ENM impacts on plants in the field under natural conditions should be conducted. Meanwhile, ENMs can enter organisms, transport and accumulate in plant tissues even in fruit, and then influence human health through food web. However, there is very limited understanding on the extent of ENMs entry into the food web and the resulting implications on environmental and human health. Therefore, the impact of ENMs on plant and microorganisms at different growth periods and their eventual accumulation within food crops should be comprehensively explored. (5) The long-term observation on the ENM toxicology is important in that they provide a more realistic and holistic approach for determining the potential risk of ENMs on soil health and microbial functions, as well as on the physiological and yield responses of plants. Furthermore, the measures, use of functional soil microorganisms (such as AMF or *Azotobacter*), or addition of exogenous substances could alleviate the harmful effects of ENMs. The applications of organic fertilizer can influence metal behavior in soil and subsequently alleviate ENM toxic effect. Most importantly, it is necessary to understand the implications of crop production, food quality, and human health when exposed to ENMs.

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Advancement of Nanotechnology Applications on Plant Nutrients Management and Soil Improvement

12

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Abstract

Food security is one of the major concerns for all developing countries of the world. Even though we had attained the highest food surplus for feeding every individual with the help of technology advancement like green revolution, we may not able to feed the burgeoning population adequately in coming years due to stagnant crop productivity. Furthermore, widespread existence of nutrient deficiency in soils had resulted in great economic loss for farmers and significant decrease in nutritional quality and quantity of grains for human beings and livestock. Natural source of nutrients like organic manures and external source of nutrients, viz. fertilisers, are considered as the two eyes in plant nutrient management in which fertilisers hold the centre of attraction in recent years for enhancing the agricultural production. However, their nutrient use efficiency is still very low due to numerous pathways of losses such as leaching, denitrification, microbial immobilisation, fixation and runoff. So, refinement of fertiliser particles through advanced technology of nanoscience is mandatory for better usage of fertilisers without any means of losses and increase the fertiliser use efficiency and nutrient uptake ratio. Nanotechnology is a novel, innovative and interdisciplinary scientific approach that involves the design, development and application of materials and devices at molecular level in nanometre scale, i.e. at least one dimension ranges in size from 1 to 100 nanometres (nm). Nanoparticles have small size, large surface to volume ratio, higher chemical reactivity, enhanced solubility and unique magnetic and optical properties. Nanotechnology-based fertilisers, i.e. nanofertilisers, are very popular among the researchers and fertiliser industries due to their controlled and targeted delivery mechanism and can able to improve the crop productivity by enhancing the seed germination, seed-

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ling growth, photosynthetic activity, energy metabolism, protein synthesis and enzymes-related functions. Apart from that, nanotechnology-based soil-binding products are helpful for improving the soil water management and retarding the soil erosion. In this chapter, advanced researches and potential applications of nanotechnology on plant nutrient management and soil improvement have been assessed.

Keywords
Nanofertilisers • Plant nutrients • Soil management • Metal nanoparticles

12.1 Introduction

Since time immemorial, agriculture is the backbone of national economy particularly in developing countries, with more than 60% of the population reliant on it for their livelihood (Brock et al. 2011). Nowadays, it's facing numerous challenges such as climate change, reduction in cultivable land due to urbanisation and low productivity of agricultural crops with higher input cost that leads to poverty and malnutrition. Among these challenges, lower crop productivity and higher input cost is the main culprit for farmer's economic loss in India. So, many factors are involved in lower productivity of agricultural crops of which declining soil fertility and mismanagement of plant nutrients are considered as an important yield limiting factors. Approximately, more than 90% of Indian soil samples exhibited low nitrogen and phosphorus content, while 50% of soil samples were low in potassium. But these nutrients are highly essential for better plant growth and development and higher yield and quality. Likewise, among the micronutrients, zinc (49%) and boron (33%) are the most deficient nutrient as compared to other nutrients, viz. molybdenum (13%), iron (12%), manganese (5%) and copper (3%) (Singh 2008). These multi-nutrient deficiencies in soil along with poor soil organic matter, lower fertiliser response ratio and imbalanced fertilisation cause stagnant level of crop productivity. However, external source of nutrients in the form of fertiliser grants more than 50% of improvement in crop productivity (Samra and Sharma 2009). But the nutrient use efficiency by crops is very low due to the loss of nutrients through fixation, leaching, volatilisation and microbial mineralisation. It has been estimated that around 40–70% of nitrogen, 80–90% of phosphorus, 50–70% of potassium and more than 95% of micronutrient content of applied fertilisers are lost in the environment and could not reach the plant which causes not only large economic and resource losses but also very serious environmental pollution. Therefore, to increase the nutrient use efficiency and improve the crop productivity from stagnant level, alternate advanced technology is urgent need of the hour.

As like the Stone Age, Bronze Age and Iron Age in human history, nowadays Nano Age is included in the human life. Nano Age means the period in which nanomaterials usage and nanoscience development studies are conducted. Nanotechnology, a promising interdisciplinary science has already been adopted by various sectors like medicine, pharmaceuticals, electronics and energy. But recently, nanotechnology has stepped into agriculture to revolutionise the field with new concepts, ideas and tools for maximising the productivity and reduce the poverty. Applications of nanotechnology in agriculture is in the nascent stage and theoretical, but it has the power to change the whole agriculture and food sector in coming years. This novel scientific approach has the potential to advance agricultural productivity through various techniques involving genetic improvement of plants, delivery of genes and drug molecules to specific sites at cellular levels, nano-array-based gene technologies for gene expressions in plants and animals under stress conditions; protect the seed from diseases and pathogen; separate the unviable and infected seed and maintain the genetic purity during seed production, early and rapid disease and pest detection by using nanosensors and controlled and smart delivery systems for agrochemicals like fertilisers and pesticides (Chinnamuthu and Boopathi 2009). In food sector, fortification of nutrients, antioxidants, vitamins and food supplements in food and identification and detection of the presence of any number and kind of bacteria and pathogens rapidly and accurately to keep the food fresh for long time can also be achieved by small particulate nanotechnology.

Considering the aforesaid points, the advanced technology, i.e. nanotechnology, has also come to revolutionise the fertiliser industry by making the fertiliser as ‘smart fertiliser’ through smart delivery systems in order to improve fertiliser formulation by minimising nutrient loss and increased uptake in plant cell, for which slow or controlled release fertilisers can be developed by using clay minerals, polymers, nanocomposites (hybrid polymer and clay minerals) and metal oxides through various methods like nanoencapsulation, spray drying, core shell preparations and electrospinning techniques. Likewise, carbon and metal oxide based engineered nanoparticles are obtaining much attraction on plant nutrient and soil management studies. Moreover, smart sensing techniques to assess the soil moisture, pH, temperature, nutrient deficiency and plant health can be accelerated through nanoscience. However, care should be taken on adoption and exploitation of potentiality of nanofertilisers due to the ethical and safety issues.

12.2 Definition of Nanotechnology

The word “nano” comes from Greek that means “dwarf,” and “technology” means visualise, characterise, produce and manipulate the matter of the size into 1–100 nm. Royal Society and Royal Academy of Engineering (2004) defined that “Nanotechnology is the Design, Fabrication and Utilization of materials, structures, devices and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale in At Least One Dimension”. National Nanotechnology Initiative, 2007, emphasised that “Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometres, where unique phenomena enable novel applications”. Nanotechnology employs nanoparticles (NPs) having one or more dimensions in the order of 100 nm or less (Auffan et al. 2009). Other authors refer to nanoparticles as colloidal particulate systems with size ranging between 10 and 1000 nm (Nakache et al. 1999). Nanoparticles are having wonderful properties like smaller size, i.e. nanometre scale, higher surface to volume ratio and greater surface reactivity with unique quantum size effects like mechanical, electrical, optical, magnetic, thermal stability and catalytic activity (Ghormade et al. 2011). The nanoparticles differ substantially from bulk materials; in fact, at this scale, matter behaves differently from the laws of applied quantum physics creating new objects with different properties (Maurice and Hochella 2008). There are two approaches for nanoparticle synthesis: one is top-down approach such as milling, high pressure homogenisation and sonication, and second is bottom-up approach that involves reactive precipitation and solvent displacement (Sasson et al. 2007).

12.3 History of Nanotechnology

Nanotechnology and nanoproducts are not new to the world. Before coining the term and processes/methods or principles of nanotechnology, people were coming across the nanosized things without understanding the nature of the products and processes. In ancient period, Egyptians used lead sulphide nanocrystals to dye their hair (5 nm similar to PbS quantum dots), and during the middle ages, different sizes of gold nanoparticles were used to produce different colours in stained glass windows in European churches for high perfection. Likewise, high-strength damask steel with nanofibrous structure and multicoloured Licurg’s bowl in British museum that contains gold nanoparticles are examples of ancient nanoproducts acquired with the unique properties of nanoparticles.

But later, the original ideas and concepts behind nanoscience and nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by Nobel Laureate physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (Caltech) on December 29, 1959. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, Professor Norio Taniguchi (1974), a researcher at the University of Tokyo, Japan, coined the term “nanotechnology” while engineering the materials precisely at the nanometre level and exploring the ultraprecision machines. Finally, the modern nanotechnology has begun with the invention of scanning tunnelling microscope that made it possible to see the individual atoms and manipulated chemical and biological molecules.

12.4 Nanotechnology on Plant Nutrient Management

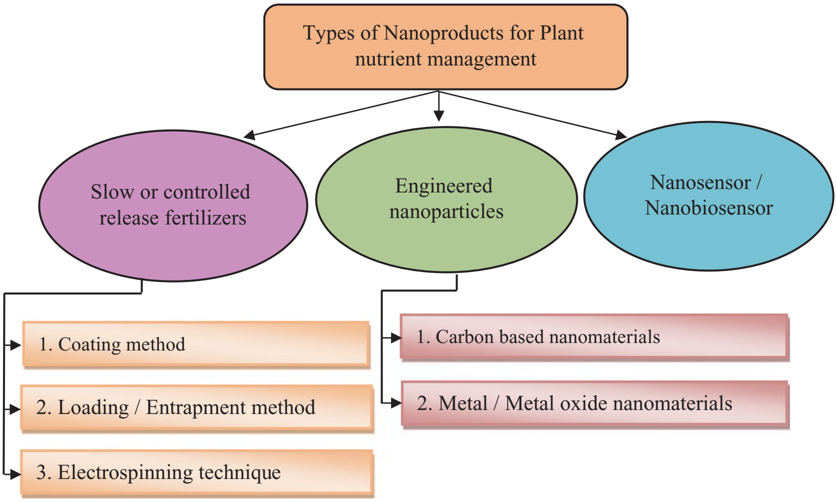
According to Cui et al. (2011), nanotechnology-based fertilisers are having the following advantages.

	Properties	Conventional fertilisers	Nanofertilisers
1.	Solubility and dispersion of mineral micronutrients	In plant nutrient management studies, water-soluble micronutrient fertilisers in the form of sulphate and nitrate have been used for increasing the crop productivity and quality. Even though these types of fertilisers are easily soluble in nature, it contains lower amount of nutrient content than insoluble form of oxide-type fertilisers like zinc, iron, copper and manganese oxides. Moreover, the particle size of the conventional fertilisers is very large, and the nutrients could not be taken up by the crop easily	Due to the advanced method of nanotechnology, oxide form of fertilisers that contains higher nutrient content can be converted into soluble form by reducing their size, shape and soluble nature. So, the bioavailability of the micronutrient can be enhanced by increasing the solubility and reducing the fixation ability in the soil
2.	Nutrient uptake efficiency	The conventional fertiliser sources of macro- and micronutrients are lost via leaching, fixation, volatilisation and microbial mineralisation, so the nutrient use efficiency and uptake ratio will be poor	The nanotechnology-based fertiliser can help to increase the nutrient use efficiency and uptake ratio because of the smaller size of the particle that can easily penetrate into the root and leaf cuticular cells through soil and foliar applications, respectively
3.	Controlled release modes	In convention, we could not avert the loss of nutrients due to the sudden burst of nutrient release at once either may through soil or foliar. Not only can create the problem for plant growth and yields due to poor nutrient use efficiency and toxicity effects but also give the high impacts on economic and resource losses, environmental pollution and ecological balance of soil	Nanoencapsulated slow and controlled release fertilisers supply the nutrients in precisely controlled manner over a period of time and improve the nutrient use efficiency. Here, water-soluble fertilisers are coated or loaded with the nanosized polymers, clay minerals and metal oxides. Surface coatings of nanomaterials on fertiliser particles hold the material more strongly due to higher surface tension than the conventional surfaces and thus help in controlled release (Brady and Weil 1999).
4.	Effective duration of nutrient release	Macro- and micronutrients are very essential to complete the life cycle of the plant. For entire plant growth period, nutrients are highly required, but deficiency symptoms of nutrients at the end of growing season occur due to excess release of nutrients at the time of delivery and beginning of plant growth stage and soon lost through leaching, fixation, volatilisation and surface runoff	The slow or controlled release nanostructured formulations are best for controlled release of nutrients for prolonged period of plant growth, which is not only favour for better yield but also reduce the loss of nutrients and in turn reduce the environmental pollution

(continued)

	Properties	Conventional fertilisers	Nanofertilisers
5.	Loss rate of fertiliser nutrients	In conventional method of fertiliser application, a meagre fraction only reaches to the target site and the remaining portions, i.e. 40–70% of nitrogen, 80–90% of phosphorus, 50–90% of potassium and more than 95% of micronutrient content of applied fertilisers, are lost in the environment and causes substantial economic losses	The encapsulation technique in nanofertilisers helps in reducing the nutrient loss rate significantly

12.5 Different Types of Nanoproducts for Plant Nutrient Management



12.5.1 Slow or Controlled Release Nanofertilisers

Best nutrient management practices involve 4 "R's, viz. right source of fertilisers, right time, right rate and right methods for enhancing the production and profitability". Fertilisers play a pivotal role for maximising the agricultural production; particularly, water-soluble and quick-release fertilisers are being used by the farmers in general, though it contains higher amount of nutrients but it releases the nutrients very quickly and lost through various pathways, viz. leaching, volatilisation, fixation, runoff and microbial mineralisation that creates the lower nutrient use efficiency. About 40–70% of nitrogen, 80–90% phosphorus and 50–70% potassium of the applied normal fertilisers are lost to the environment and cannot be absorbed by plants, which causes not only large economic and resource losses but also very serious environmental pollution. To address these problems, slow and controlled release technology in fertiliser is considered as a suitable method to provide a steady and continuous supply of nutrients throughout the plant growth period without having the excess hazardous release of nutrients. The technology is designed for the fertiliser to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant (Junejo et al. 2011). The quantity and duration of the plant nutrient release mainly depend upon the coating materials of controlled release fertiliser. According to Trenkel (1997), controlled release fertilisers (CRFs) must meet the following three criteria: (1) less than 15% of the CRF nutrients should be released in 24 h; (2) less than 75% should be released in 28 days, and (3) at least 75% should be released by the stated release time (40–360 days). Recently, nanotechnology has become a handy tool to the fertiliser industry for making the fertiliser as 'smart fertiliser' through smart delivery systems, in which slow or controlled fertilisers can be developed by using the methods like encapsulation technique through coating, coacervation, sol-gel preparation, spray drying, core shell preparation, electrospinning, etc., in which various materials like clay minerals, polymers, porous structured metal oxides and mesoporous silica are used.

12.5.2 Encapsulation of Nanomaterials Through Coating Method

Controlled/slow release fertilisers are excellent alternative to soluble fertilisers which can reduce the application rate and application frequency by releasing their nutrient gradually to coincide with the nutrient requirement of the plant. Recently, coating of fertilisers either through synthetic or natural polymers has got an attraction in slow delivery technique of agrochemicals. Wu et al. (2008) prepared the double-coated slow release NPK compound fertiliser with superabsorbent and water retention by crosslinked poly(acrylic acid)/diatomite containing urea (the outer coating), chitosan (the inner coating) and water-soluble granular fertiliser NPK (the core). This product with excellent slow release and water retention capacity, being nontoxic in soil and environmental friendly, could be especially useful in agricultural and horticultural applications. Corradini et al. (2010) studied the incorporation of NPK fertiliser sources such as urea, calcium phosphate and potassium chloride into chitosan with methacrylic acid (MAA) nanoparticles for controlled release of nitrogen, phosphorus and potassium nutrients. Encapsulation of urea and phosphorus fertilisers with sulphur nanocoating ($\leq$100 nm layer) are useful slow release fertilisers; also the sulphur contents are beneficial especially for sulphur-deficient soils (Brady and Weil 1999). The stability of the coating reduced the rate of dissolution of the fertiliser and allowed slow sustained release of sulphur-coated fertiliser. Fernando et al. (2010) studied release rates of phosphate through the coating from calcium phosphate fertiliser pellets coated with mixtures of wax and nanocalcium oxide and found that the increasing content of nanocalcium carbonate in the wax coating layer and decreasing pH increased the nutrient transfer rate to the surrounding.

Nowadays, clay minerals are being used for encapsulating agrochemicals such as fertilisers, plant growth promoters and pesticides due to their high surface area, large adsorption power, easily modified surfaces and their colloidal nature. Clay minerals are natural and relatively cheap components of soils and being used as the reservoir and cache of nutrient elements. The layers of nanostructured clay minerals have large active surface area which is exploited to provide enhanced surface interaction with fertiliser elements. Man et al. (2004) intercalated urea into the montmorillonite layers to prepare controlled release urea-based fertiliser. Moreover, these clay minerals are used to hybridise with polymers for producing polymer-clay nanocomposite, which is considered as another potential area in slow release fertiliser concept. The hybridisation takes place between inorganic clay minerals, viz., montmorillonite, bentonite and kaolinite with organic superabsorbent polymer that leads to changes in composition and structure of the product which impart higher water holding capacity, swelling rate and slow release property. Studies with pillared clay-modified phosphate fertilisers reported decreased fixation and increased bioavailability of soil phosphorus (Basak et al. 2012). Coating and cementing of nano- and sub-nanocomposites are capable of regulating the release of nutrients from the fertiliser capsule (Liu et al. 2006). A patented nanocomposite that consists of N, P, K, micronutrients, mannose and amino acids that increase the uptake and utilisation of nutrients by grain crops has been reported (Jinghua 2004).

12.5.3 Encapsulation of Nanomaterials Through Loading (Entrapment)

Due to some shortfalls of encapsulation of nanomaterials through coating, i.e. difficulty of releasing the active ingredient from the coating or sudden bursting of active material from the coating which means the release and dissolution rates of water-soluble fertilisers always depend on the coating materials, a novel nutrient delivery system, i.e. loading of nanomaterials into porous hollow materials like silica, clay minerals and metal oxides, can be adhered. The hollow structure with pores in the shell allows a high loading of nutrients and controls the release rate to achieve the sustained release. The porous-type clay minerals like zeolites particularly clinoptilolite species are considered as a vehicle for efficient nutrient delivery, so zeolite-based nanofertiliser are very popular among researchers and fertiliser industries. Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, with a three-dimensional lattice, furrowed by an inner network of pores and channels. Zeolites have a high cation exchange capacity and have often been used as inexpensive cation exchangers for various applications (Breck 1974). This natural super porous mineral (part of group of hydrated alumina silicates) carrying a negative charge can be used to trap positive cations such as ammonium and potassium for slow and steady release of nutrient during the crop growth period. Zeolite surface charge modification can be achieved by addition of surfactant hexadecyltrimethylammonium bromide (HDTMABr) to ensure the negatively charged elements like sulphate and phosphate entrapment (Preetha et al. 2014). The clinoptilolite was found to have high potential as a vehicle for nitrogen, phosphorus and potassium fertilisers because it can decrease negative impacts on the environment and increase fertiliser efficiency. Application of clinoptilolite-NH_4 resulted in a considerable increase of *Lolium multiflorum* yield and enhanced nitrogen uptake efficiency, possibly due to its ability to retain and slowly liberate NH_4^+ ions. Manikandan and Subramanian (2014) synthesised the nanoporous zeolite-based nitrogen fertiliser of which nitrogen nutrient loading efficiency was 28% and releasing time of the nitrogen was up to 48 days as compared to conventional urea fertilisers. Likewise, urea-modified hydroxyapatite NPs were encapsulated under pressure into the cavities of soft wood of *Gliricidia sepium* and were tested for slow and sustainable release of N into the soil. Interestingly, N supply through this strategy was found optimum up to 60 days compared to conventional nitrogenous fertilisers, which gave more N supply to the plants in the beginning and very low at the later stage up to 30 days.

Another important research area for entrapment of fertilisers is the preparation of hollow core shell nanomaterials and nanostructures. During the last few decades, hollow core shell system has been used for loading of drugs, pesticides, herbicides and Bt toxin in biomedical and agricultural applications. As like above, different size, shape and shell thickness of hollow core shell can be prepared either by using calcium carbonate or manganese carbonate for entrapping the water-soluble fertilisers to delay and control the nutrient-releasing behaviour by reducing their dissolution rate as well as enhance the nutrient use efficiency. Recently, Yuvaraj and Subramanian (2015) prepared nanosized manganese hollow core shell encapsulated zinc sulphate fertiliser, and these Zn-fortified core shell released Zn for more than 696 h, while Zn release ceased after 408 h in zinc sulphate-fertilised soil. Moreover, the encapsulation of Zn using a manganese hollow core shell improved Zn use efficiency by rice while reducing the loss of nutrients and minimising environmental pollution.

12.5.4 Electrospinning of Nanofertilisers

Electrospinning is a unique approach using electrostatic forces to produce ultrafine fibres with diameters in the range of micro- to nanometre scale and can be applied to all soluble or meltable polymers. Due to the simplicity and straight forwardness of this process, it has been developed from a single fluid to two fluids (coaxial and side-by-side electrospinning) which create new types of complicated nanofibres with well-defined microstructures, novel morphologies and/or new functions. There are several researches and patents related to electrospinning for controlled release applications in the past several years. Most reports focused on biomedical and pharmaceutical applications. Recently, Castro-Enríquez et al. (2012) prepared the prolonged-release system of urea from wheat gluten by the electrospinning technique. The release of urea during the first 10 min was very fast, and then the rate of release decreased as it reached equilibrium at 300 min, with a total of ≈98% urea released. Kampeerapappun and Phanomkate (2013) synthesised the core-shell fibres with polyhydroxybutyrate (PHB) as the shell and polylactic acid (PLA) mixed with fertiliser as the core by coaxial electrospinning. At a fixed flow rate of shell solution, the core-shell electrospun fibre mats exhibited a lower flow rate of core solution, causing a lower release rate of the fertiliser. These core-shell structures are suitable to control the manner and timing of fertiliser delivery, and an electrospun mat can release fertiliser for 1 month without degradation. Moreover, both polymers are biodegradable matrices so that they become environmentally friendly.

12.6 Engineered Nanoparticles

In today's modern world, engineered nanoparticles (ENPs) are becoming an important component of daily life, and their usage has been increased rapidly in cosmetics, medicine, energy, machinery and agriculture sectors. Engineered nanoparticles are intentionally produced and designed with very specific properties related to shape, size, surface properties and chemistry. These properties are reflected in aerosols, colloids and powders. ENPs are divided into four categories according to USEPA: carbon-based materials, metal-based materials, dendrimers and composites. Among them, metal oxide nanoparticles are receiving attention in a large variety of applications; efforts are underway in many laboratories to understand the potential for ecotoxicity. One major advantage of the engineered nanoparticles in agriculture is insoluble form of chemical compounds with higher nutrient content that can be converted into relatively soluble form by reducing their size and changing their shape of the molecules through physical, chemical and biological method of preparations. Hence, nutrient use efficiency can be increased.

12.6.1 Carbon-Based Nanomaterials

Carbon is the non-metallic element and its history is as old as the human civilisation. The carbon materials like wood charcoal and activated charcoal have been used by Indians and Egyptians for water purification and decolourisation since 3750–1500 BC. In recent years, carbon-based nanomaterials have been recognised as the powerful tool in all the sectors like material, optical devices, quantum computer, removal of biological contaminants, molecular switch, tissue engineering, pharmacy and medicine or carrier in drug delivery system. A wide variety of carbon-based nanomaterials such as fullerene, fullerene cages, single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) have been prepared, of which fullerene (Hollow sphere carbon molecule – 60 C) is the first and foremost synthesised nanomaterial by Richard Smalley, Robert Curl, James Heath, Sean O'Brien and Harold Krotoin 1985 at Rice University. Later, MWCNTs followed by SWCNTs were synthesised under defined conditions to control the size and diameter of the tubes.

Recently, carbon nanomaterials are exposed into agriculture to increase the crop production. Kole et al. (2013) found that bitter melon seeds treated with fullerene increased the fruit yield by 112–128%, biomass and phytomedicine contents like cucurbitacin B (74%), lycopene (82%), charantin (20%) and insulin (91%). Khodakovskaya et al. (2009) reported that MWCNTs can penetrate tomato seeds and increase the germination rate by increasing water uptake. The MWCNTs increased the seed germination (90%) as compared to control (71%) and plant biomass (20 days old). Similarly, Srivastava and Rao (2014) concluded that germination percentage, growth and biomass production of wheat, maize, peanut and garlic were increased by application of 50 ppm of MWCNTs, which can able to penetrate the seed coat by creating new pores, thereby enhancing water uptake. However, some of the findings showed that carbon-based nanomaterials do not have any significant effect on crops like *Arabidopsis* (Lin et al. 2009), rice (Xm et al. 2009) as a consequence of accumulation of reactive oxygen species (ROS) and decrement of the dry weight, chlorophyll content and superoxide dismutase activity (SOD) that caused cell damage and death of plants. Finally, the experimental results either it is positive or negative concluded that the effects of carbon-based nanomaterials like fullerene, single or multi-walled carbon nanotubes on different crop plants are very different and differently reacts, but it may change in the presence of other substances or the organic material already present in the medium. Some of the findings reported that functionalised carbon-based nanomaterials did not show any apparent toxic effects on crop plants. Canas et al. (2008) studied the effects of functionalised and non-functionalised SWCNTs on six plants, namely, cabbage, carrot, cucumber, lettuce, onion and tomato. Likewise, Khodakovskaya et al. (2009) concluded that the lower concentration of oxidised MWCNTs had better effect on the mustard seed germination than the carbon nanotubes alone.

12.6.2 Metal Oxide Nanoparticles on Seed Germination

Different types of nanomaterials on seed germination and plant growth with the aim of better crop production have been studied by various researchers. Metal and metal oxide nanoparticles like zinc, iron, titanium, gold, copper, aluminium and silver are highly influencing the seed germination and plant growth, that can be either positive or negative. Zheng et al. (2005) reported that nano-TiO_2-treated spinach seeds-produced plants (30 days old) had 73% more dry weight, three times higher photosynthetic rate and 45% increased chlorophyll ‘a’ formation as compared to control. Mahmoodzadeh et al. (2013) found that TiO_2 nanoparticles enhanced seed germination and promoted radicle and plumule growth of canola seedlings. They concurred that the nanosize of TiO_2 might have increased the seed stress resistance and promoted capsule penetration for intake of water and oxygen needed for fast germination. The highest seed germination, seedling vigour, seedling length and seedling dry weight were achieved by application of nano-TiO_2 on maize (Sani 2012), tomato (Giordani et al. 2012), onion (Raskar and Laware 2013) and flax seed (Clement et al. 2013). Several researches related on ZnO nanoparticles on seed germination and seedling growth have been conducted in various crops like mung bean, gram and peanut. The performance of ZnO nanoparticles on crops highly depends upon the size, shape and dosage of the particles. Most of the studies revealed that application of ZnO nanoparticles promptly enhanced the seed germination percentage, root growth development and chlorophyll content at lower concentration (Mahajan et al. 2011; Prasad et al. 2012; Sedghi et al. 2013; Jayarambabu et al. 2014; Gokak and Taranath 2015). But very few study only devoted to the influence of iron oxide on seed germination revealing the stimulatory effect on the seed germination indices and seedling growth. Feizi et al. (2013) found that 100 ppm iron oxide nanoparticles showed the greatest germination rate, i.e. 41%, and reduced the mean germination time (MGT) by 38.5% and root biomass of wheat crop; it may be due to stimulatory effect of iron oxide nanoparticle by increasing the better uptake of water and oxygen. But when increasing the nanoparticle concentration above 100 ppm, seed germination rate and root weight of the plant may get reduced.

Silicon (Si) is a critical element for a number of metabolic and physiological plant activities. Lu et al. (2002) showed that a combination of nanosized SiO_2 and TiO_2 could increase nitrate reductase enzyme in soybean, increase its abilities in absorbing and utilising water and fertiliser, encourage its antioxidant system and actually hasten its germination and growth. Rad et al. (2014) reported that application of nanoscale SiO_2 at 400 ppm concentrations increased the seed germination, root and shoot elongation and relative water content in maize. Particularly leaf chlorophyll a and b and carotenoid content were increased in treated plants irrespective of the concentrations as compared to control. Azimi et al. (2014) revealed that application of SiO_2 nanoparticles significantly increased seed germination of tall wheatgrass from 58% in control group to 86.3 and 85.7% in 40 and 60 mg/L, respectively. Also they concluded that seed prechilling in combination with SiO_2 nanoparticles largely broke the seed dormancy for tall wheatgrass (*A. elongatum*). Different types of metal nanoparticles, viz. silica (Si), gold (Au), palladium (Pd), and copper (Cu), were studied on lettuce seed germination by Shah and Belozerova (2009) and they reported that nanoparticles of Pd and Au were at lower concentrations, Si and Cu were at higher concentrations and combinations of Au and Cu had a positive influence on seed germination and root shoot ratio of lettuce seedlings.

But, Lin and Xing (2007) evaluated the phytotoxicity of nanomaterials, i.e. negative effect (MWCNTs, $Al_2O_{3,}$ ZnO, Al and Zn), on germination of radish, rape, canola, ryegrass, lettuce, corn and cucumber. They revealed that higher concentrations (2000 mg/L) of nanosized Zn (35 nm) and ZnO (20 nm) inhibited the germination in ryegrass and corn, respectively. Root length of studied species was also inhibited with the use of 200 mg/L nano Zn and ZnO. Similarly, nano-Al and nano-Al_2O_3 affected root elongation of rye grass and corn, respectively, whereas nano-Al facilitated the radish and rape root growth. Overall, the above experimental results showed that smaller dosage of metal oxide nanoparticles produced the higher biomass and yield than higher dosage of metal oxide nanoparticles which inhibits the plant growth rate; besides the phytotoxicity effect can be prevented by coating the nanoparticles with biocompatible products (Tripathi et al. 2016; Shweta et al. 2016; Singh et al. 2016).

12.6.3 Foliar Application of Metal Oxide Nanoparticles

Apart from the various researches on sorption and release characteristics of the nutrients from slow or controlled release nanofertilisers in soil, penetration and transportation of nanoparticles in aerial parts of the plants have been discussed nowadays by applying the nanonutrients through foliar spray which can also be enabled as a promising nanofertiliser application method for increasing the crop productivity. In fertiliser management programme, micronutrients like Zn, Fe, Cu and Mn are as essential as the macronutrients (N, P and K) to attain the higher yield and complete the plant growth cycle. Metal oxide-based micronutrient fertilisers got the special attention because of the rapid growing science, i.e. nanotechnology. Normally, Zn is an essential micronutrient that plays many important roles in various physiological and metabolic processes in all living organisms. It functions as a cofactor for over 300 enzymes and proteins involved in cell division, nucleic acid metabolism and protein synthesis. Metal oxides of Zn (ZnO) is utilised in a range of applications such as sunscreens and other personal care products, solar cells, photocatalysis, biosensors, and electrodes. Zinc oxide (nano-ZnO) is categorised as commonly used metal oxide ENPs and can be developed by all the three methods like physical, chemical and biological methods. Raliya and Tarafdar (2013) biologically synthesised zinc oxide nanoparticle with the average diameter of 3.8 nm in at least one dimension by using extracellular fungus *Aspergillus fumigatus* TFR-8, and they found greater improvement in shoot and root growth, chlorophyll (photosynthetic pigment), total soluble leaf protein content, rhizospheric microbial population and P nutrient mobilising enzymes (phytase, acid and alkaline phosphatase) by the application of biologically synthesised ZnO nanoparticle at 10 mg/L concentration on 2-week-old plants. The gum content and its viscosity in seeds of cluster bean at crop harvest were also significantly improved by application of nano-ZnO.

Next important micronutrient for plant growth is iron, which plays a critical role in chlorophyll formation, photosynthesis, enzymes and respiration activities of plants. Commonly, water-soluble iron fertilisers like iron sulphate and chelated form of iron are used for plant growth and development. Zareie et al. (2011) found that foliar application of iron sulphate fertilisers increased the peanut yield (38–42%) in alkaline soils. Due to nanotechnology science, the insoluble forms of metal oxide like iron oxides can be converted into soluble form by reducing their particle size and increasing their solubility rate which may get the importance in plant nutrient management due to the beneficial property of higher nutrient content. Nanoparticles have high reactivity because of more specific surface area, more density of reactive areas or increased reactivity of these areas on the particle surfaces. Foliar application of iron oxide (Fe_2O_3) nanoparticle increased the chlorophyll content, antioxidant enzymes particularly catalase activity and yield of the peanut crop (Liu et al. 2005). Similarly, Sheykhbaglou et al. (2010) reported that application of 0.75 g/lit of nano-iron oxide facilitated the nutrient transfer to aerial plant parts and increased the dry weight of leaf and pods thus may cause for enhancing the total soybean yield. Ghafari and Razmjoo (2013) found that foliar spray of 2 g L^{-1}

nano-iron oxide was more effective on increasing the wheat yield than that of other iron sources like iron sulphate and iron chelates.

Beside the above-mentioned metal oxide nanoparticles that supply essential nutrients to plants, some other nanoparticles, viz. TiO_2, Al_2O_3, SiO_2, Au and Ag NPs, were found to have beneficial effects on plant growth. Although titanium does not belong to essential plant nutrients, application of TiO_2 NPs was found to stimulate ribulose 1,5-bisphosphate carboxylase (rubisco) activity; increase photosynthesis efficacy; regulate enzymes activity involved in nitrogen metabolism such as nitrate reductase, glutamate dehydrogenase, glutamine synthase and glutamic-pyruvic transaminase that helps the plants to absorb nitrate; and also favour the conversion of inorganic nitrogen to organic nitrogen in the form of protein and chlorophyll, thereby enhancing plant growth and development (Jaberzadeh et al. 2013 and Mishra et al. 2014). Addition of 0.25% TiO_2 (rutile) NPs that caused stimulation of photosynthetic electron transport resulting in increased oxygen evolution rate in spinach chloroplasts and enhanced activities of Mg^{2+}ATPase and chloroplast coupling factor ICF1-ATPase on the thylakoid membranes were observed. Application of titanium dioxide (TiO_2) on food crops promoted plant growth, increased the photosynthetic rate, reduced disease severity and enhanced yield by 30% (Agarwal and Rathore 2014).

Application of a mixture of SiO_2 and TiO_2 NPs at low concentrations increased the activity of nitrate reductase in the rhizosphere of soybean, resulting in accelerated soybean germination and growth. Nano-SiO_2 enhances the plant growth and development by increasing gas exchange and chlorophyll fluorescence parameters such as net photosynthetic rate, transpiration rate, stomatal conductance, PSII potential activity, effective photochemical efficiency, actual photochemical efficiency, electron transport rate and photochemical quench (Siddiqui et al. 2014; Xie et al. 2011). Under salinity stress, nano-SiO_2 improves leaf fresh and dry weight, chlorophyll content, proline, free amino acids and antioxidant enzymes activity (Kalteh et al. 2014). In earlier times, researchers found that some of the submicron-sized metal oxide particles like aluminium are highly toxic to plant growth. This fact was supported by Kinraide et al. (1992). They reported that application of high concentration of Al_2O_3 can stunt root growth and induce damage in cucumber, corn, carrot, cabbage and soybean. But in recent years, even though Al_2O_3 nanoparticles have the potential to affect the crops, when it is coated, the phytotoxicity effect will be reduced due to less contact of the particle directly. This was proved by Yamamoto et al. (2001). Gold nanoparticles have been extensively studied in recent years due to their abundance of potential applications to biological systems. In recent years, gold nanoparticles are being used for delivery of genetic material, i.e. DNA into plants and detection of plant viruses along with seed germination purpose. Some of the researchers found that gold nanoparticles (AuNP's) induces toxicity in the plants (Shah and Belozerova 2009) and others proclaimed the beneficial effects of gold nanoparticles on plants such as lettuce and cucumber (Barrena et al. 2009), *Brassica juncea* (Arora et al. 2012) and *Gloriosa superba* (Gopinath et al. 2014).

Silver nanoparticles (AgNPs) are one of the commercially used nanoparticles particularly in cosmetics, food and medicine due to its properties of antibacterial, antifungal and antioxidant. Many studies on AgNPs have been documented on microbial and animal cells; however, only a few studies were done on plants. Krishnaraj et al. (2012) and Savithramma et al. (2012) found that biologically synthesised Ag nanoparticles on crop plants showed a significant effect on seed germination and induced the synthesis of protein and carbohydrate and decreased the total phenol contents and catalase and peroxidase activities. Nejatzadeh-Barandozi et al. (2014) reported that foliar application of either nanosilver or silver nitrate increased seed yield due to increase in inflorescence number per unit area and decreased the seed abscission through reduced ethylene production in basil plant. In seed germination tests, most of the researchers found that silver nanoparticles are highly favourable for increasing the root length, root fresh weight and root dry weight and root elongation along with significant improvement of seed germination percentage.

12.6.4 Uptake Mechanism of Nanomaterials

Normally, essential and non-essential plant nutrients are easily absorbed by the plants, but nanomaterials suspended in water may be selectively absorbed or rejected by plants. Engineered nanoparticles can reach and interact with the plants through direct application via soil or foliar, accidental release, contaminated soil/sediments and atmospheric fallouts which results some significant positive or negative effects on food crops and food chains. In recent years, study on nanoparticles uptake, accumulation, translocation within plant parts and biotransformation of nanoparticles via above-ground parts (leaf) and below-ground parts (root and seed) has been initiated. Some of the studies showed that nanoparticles have the ability to penetrate the cell walls and plasma membranes of the epidermal layers of roots and then enter into the vascular tissues (xylem) of the plant. The smaller size of the nanoparticle are expected to pass through the cell wall which may be due to porous network of polysaccharide present in the cell wall (pore size of cell wall is 3–8 nm in diameter) that act as the natural sieve, but larger nanoparticles aggregates at the surface. However, Navarro et al. (2008) revealed that the nanoparticles may induce the formation of new and large-size pores when nanoparticles come in contact with cell walls which allow the internalisation of larger nanoparticles.

Carbon nanomaterials like carbon nanotubes, fullerene, fullerol and grapheme oxide are used in foliar spray, seed treatment and soil applications. Khodakovskaya et al. (2009) found the ability of carbon nanotubes particularly MWCNT produce pores on the tomato seed coat that favoured water uptake as well as tomato seed germination and growth of seedlings. Regarding the uptake of carbon nanomaterials via roots, Cifuentes et al. (2010) observed that Magnetic carbon-coated nanoparticles ranging from 5 to 50 nm with an average hydrodynamic diameter of 200 nm were absorbed by the roots and then translocated to the xylem vessels up to the leaves (in wheat up to the trichomes), with a different efficiency depending on the species. Moreover, carbon nanotubes either may accumulate on the root surface of the cell walls or may translocate into aerial parts of the plant including flowers and fruits. Accumulation of MWCNTs and SWCNTs was observed on the root surface of several crop plants including tomato, wheat, cabbage, lettuce, carrot, cucumber, onion, and rice. Organic materials present in the solution with carbon nanotubes can facilitate to absorb the nanomaterials and transport them into the aerial parts of the plants due to capillary action. This carbon nanomaterial is genetically transmitted to the next generation of plants. The two consecutive generations of rice seeds grown showed the accumulation of C70 nanomaterial at different stages and different parts of the plant followed by insertion of C70 nanomaterial in the first generation and then subsequent transmission to the progeny in the second generation (Rico et al. 2011). On the basis of high-resolution transmission electron microscopy studies, it has been shown that long MWCNTs (larger than 200 nm) get accumulated in subcellular organelles, while the shorter ones (30–100 nm) were found into vacuoles, nucleus and plastids (Serag et al. 2013). But, there was no uptake of SWCNTs and were found adhered to the external surface of the main and secondary roots of the cucumber seedling (Lou et al. 2011; Yuan et al. 2011). However, fullerene aggregates were mostly present in or near the stems' vascular system and leaves, whereby the roots have been devoid of fullerene (Santos et al. 2013). It is concluded that the individual fullerenes nanoparticle enter the plant roots through osmotic pressure, capillary forces and pores in the cell walls by the intercellular plasmodesmata or by means of the greatly regulated symplastic routes. Moreover, Gao et al. (2011) and Kole et al. (2013) pointed out that smaller size of the fullerene particles, i.e. less than a pore diameter of the cell wall, could easily pass through the plasma membrane and accumulate at the interface between the cell wall and plasma membrane and also occurred between adjacent epidermal cell walls.

Foliar uptake of carbon-based nanomaterials are not well documented; however, due to some advanced methods of foliar application of SWCNTs on spinach proved the ability to cross the stomata as well as to penetrate chloroplasts and accumulate on thylakoids and stroma (Giraldo et al. 2014). More number of studies has been carried out in order to obtain the uptake and transport of metal oxide nanoparticles from root to shoot of the plant. As like above the carbon-based nanomaterials, more evidence regarding uptake of metal and metal oxide nanoparticles, viz. TiO_2, SiO_2, ZnO, Fe_3O_4, FeO, Ag and Au, through foliar, root and seed coating can be collected. The foliar epidermis is made up of cells with the exposed walls waterproofed by hydroxylated fatty acids (cutin and waxes), which form a cuticle membrane and also is provided with stomata ranging from 100 to 1300 per mm^2 consisting of two guard cells and, in which through expansion (turgor), form a pore between them ranging from 3 to 12 μm in width and 10–30 μm in length, for gas exchange purpose. The stomatal pore is the vital point for entry of foliar applied metal and metal oxide nanoparticles which succeeded over the root and seed coating method of application due to the penetrating power of metal oxide nanoparticles into the epidermis as well as underlying palisade tissue and translocating to the stems and roots of the plant. Some of the studies found that metal oxide nanoparticles have the ability to penetrate seeds without affecting the seed germination and seedling growth. Likewise, metal nanoparticles can be easily absorbed by the roots and translocate them in stems and leaves which depends on the physicochemical features of NPs, type of the plant and growth medium.

12.6.5 Nanosensor/Nanobiosensor on Plant Nutrient Management

With the advent of nanoscience and nanotechnology in diagnostic devices, nanosensors got attention in recent years in various science sectors and industries. A nanodevice or nanosensor can be simply defined as any manufactured device whose dimensions are on the scale of 1–100 nm and whose properties exploit the unique properties of nanoscale materials. Nanobiosensor is a compact analytical device/unit and called as modified version of a biosensor in which the immobilised layer of biological material like proteins, DNA/RNA, viruses, cellular lipid bilayers, microbial cells and others are in contact with the sensor that analyses the biological signal and converts into electrical signal. So much of researches found the usage of nanobiosensor in medicine for diagnostic and therapy of cancer cells. However, nanobiosensor can be effectively used in agriculture for sensing a wide variety of fertilisers, herbicides, pesticides, pathogen, moisture, soil pH and others for enhancing the crop productivity. These biosensors may have a huge impact on the precision farming methods. Nanosensors can be linked to a GPS and distributed throughout the field for real-time monitoring of disease, crop health, soil conditions and their potential problems such as soil nutrient depletion and water deficit. Networks of wireless nanosensors positioned across cultivated fields provide essential data leading to best agronomic intelligence processes with aim to minimise resource inputs and maximising output and yield (Scott and Chen 2003). Such information and signals include the optimal times for planting and harvesting crops and the time and level of water, fertilisers, pesticides, herbicides, and other treatments that need to be administered given specific plant physiology, pathology and environmental conditions. For diagnosing the nutrient deficiency in plants, nanosensors are impregnated with nanoparticles that can be used to determine the nutrient status and deficiency of the plants, which assist in taking up appropriate and timely corrective measures to reduce the yield reduction.

The USA and Australia have already exploited this technology. Certain vineyards in California have installed WiFi technology with the help of IT company, Accenture. Although the initial cost of installing such a system is high, but it is justified by the fact that it enables the best grapes to be grown which in turn produce finer wines, which command a premium price. With these nanosensors, accurate information about crop growth and field conditions including moisture level, soil fertility, temperature, crop nutrient status, insects, plant diseases, weeds, etc., can able farmer to enhance the crop productivity by making better decisions (Kumar 2011).

In recent times, microbe-based sensors have been used in the diagnosis of micronutrient particularly zinc deficiency and toxicity in soils. For example, a zinc-specific biosensor, *Pseudomonas putida* X4 (pczcR3GFP), was constructed by fusing a promoterless-enhanced green fluorescent protein (egfp) gene with the czcR3 promoter in the chromosome of *P. putida* X4. The fluorescent reporter strain detected about 90% of the Zn content in soil-water extracts of soil samples amended with Zn. The authors concluded that the biosensor constitutes an alternative system for the convenient evaluation of Zn toxicity in the environment (Liu et al. 2012). The bioavailability and toxicity of Zn in laboratory soil amended and field samples have also been assessed using a gene in *E. coli* HB101 (puCD607) as the biosensor and *E. coli* MG 1655 (pZNTlux) as the bioreporter (Maderova and Paton 2013). Next, aptamer-based nanobiosensors appear as a useful tool to study the origin and reactions of metabolites produced by living cells in crop rhizospheres and to investigate the controlled released materials applied in agriculture and medicine. The incorporation of nanodevices like aptamers in polyelectrolyte polymer films prepared by layer-by-layer assembly may have potential for applications in targeted delivery systems for the controlled release of drugs, pesticides, or other payloads such as plant nutrients (Sultan and DeRosa 2011; Zhang et al. 2013). Intelligent nanodevices or biosensors may help to detect and treat nutrient deficiencies in soils and plants by delivering the macro- and micronutrients according to the temporal and spatial nutrient requirements of crops during the growing season. Monreal et al. (2015) developed the intelligent nanofertilisers (INF) delivery platforms for micronutrients such as Zn and Fe, in which the main mechanism of nutrient release is based on the recognition and binding of a specific plant signal by a nanobiosensor housed in a polymer film which coats micronutrient (Zn, Fe, Cu and Mn) fertiliser nanoparticles or salts.

12.7 Nanotechnology on Soil Management

Nanoscience is of crucial importance to the soil science because many natural components in the soil are having nanoscale features. Different types of nonmaterial such as clays (zeolite, montmorillonite and micaceous clay), minerals like iron and manganese oxides (e.g. ferrihydrite, hematite, goethite, maghemite, lepidocrocite and magnetite) and organic materials like humic and fulvic acid are present in soils at nanoscale level (Mura et al. 2013). Manufactured or engineered nanoparticles can also be found in soils not only by application of nanomaterials in agriculture, like fertilisers, pesticides, etc., but also due to thrown out of nanoparticles containing materials as waste from various sectors like medicine, energy and other industries (Qafoku 2010).

Nowadays, nanofertilisers have a great promise for enhancing the nutrient use efficiency through smart or controlled delivery system besides reducing the soil pollution by controlling the wastage of fertilisers via leaching, run off, volatilisation and immobilisation. The slow release of nutrients into rhizosphere could be achieved by using zeolite, i.e. honey comb-like layered crystals and polymer-based materials. Zeolite is known as the best adsorbent material for heavy metals because it has the highest CEC and adsorption rates (Yeshchenko et al. 2005) and also more useful to improve water holding capacity of the soil (El-Salmawi 2007). Subramanian and

Rahale (2012) reported that the entire available Zn from zinc sulphate was exhausted after 120 h beyond which the concentration of Zn^{2+} reached below detectable limits. However, the release of zinc from nano-zeolite was continued even after 1176 h, with a concentration of 5 ppm. It interprets that zeolite acts as a reservoir of nutrients by recharging the adsorption sites with dissolved nutrients from soil and then slowly releasing the nutrients throughout the crop growth which can ensure plant development besides environmental safety. Likewise, nitrogen leaching was found to be lowered when slow release fertilisers were coated by nanomaterials such as plastic-starch composites applied to wheat (Zhang et al. 2006). The installation of nanosensors, or nanoscale wireless sensors, in farmers' field is being applied to enable the real-time monitoring of soil and the early detection of potential problems such as soil nutrient depletion and water deficit.

Soil is the soul of our life. Without soil, there will be no microbes, no plants and no human life history. So, soil and water are as important as like our eyes to the earth. In agricultural point of view, if the soil contains no water, there is a problem for plant growth and nutrient uptake functions. Recently, nanomaterials are also helpful for improving soil water management. Nanosand was developed by covering the sand with additive (DIME hydrophobic materials) to prevent water drainage below the depth of the plant roots particularly in dryland, maintain subsurface water table and support release of nutrients for plant growth (Davidson and Gu 2012). Similarly, another important soil-water enhancer is Geohumus soil-like particles that are obtained by mixing the nano-scale volcanic rock dust and clay minerals with the useful properties of super absorbent polymer at molecular level to form an inseparable new composite. This product is ideal for continuous supply of water due to the swelling capacity, and it helps to improve the water holding capacity of the soil, aeration, root penetration, biological activity and retention of nutrients for better uptake and growth of the plants particularly in arid and sandy soils.

In 2003, ETC (Erosion, Technology and Concentration) Group reported on a nanotechnology-based soil binder called SoilSet developed by Sequoia Pacific Research of Utah (USA), which is a quick-setting mulch which relies on chemical reactions on the nanoscale to bind the soil together. It was sprayed over 1400 acres of Encebado Mountain in New Mexico to prevent erosion following forest fires, as well as on smaller areas of forest burns in Mendocino County, California. Likewise, nanomembrane, i.e. nanoclay, was also developed to mitigate wind erosion, binding the soil particles to generate soil aggregates, increase the available water table and improve the moisture holding capacity for better plant growth development. Nanoclay is made up of clay minerals divided into their smallest components that are 0.7–1.5 nm thick, with a diameter of 20–300 nm and mixed with water. The test results of nanoclay applied in hot, dry, sandy soil in Egypt was an increase in yield of up to 416% while using only one-third of the normal consumption of irrigation water (Olesen 2010). Following the above approach, Iranian company, Zist Palayesh Zamin has developed the sand dunes stabilising nanomaterial which contains biopolymeric nanocoils (polylattice) to prevent environmental pollution in desert areas. Nanotechnology-based soil clean-up product was also developed by using iron nanoparticles that can able to clean up the soil from heavy metals and polychlorinated biphenyls (PCBs) contamination by injecting the soil with this product. The researcher found that nanoparticles flow along with the groundwater and decontaminate en route, which is much less expensive than digging out the soil to treat it. Also he found that nanoscale iron will remain active in the soil for 6–8 weeks, after which time it dissolves in the groundwater and becomes indistinguishable from naturally occurring iron.

When considering the nanoparticles movement in soil, size and shape of the nanoparticles influenced greatly through Brownian motion in soil pores, but it is not affected by gravitational settling force. Nanoparticles are highly mobile in porous soil because these particles, approximately 10 nm, are much smaller than soil pore spaces. Also, smaller nanoparticle has the larger surface area with higher reactivity. Over the time period or ageing of the nanoparticle, it can be coated with thin layers of other phases leading to decrease in surface area and reactivity and increased structural defects that reduce the mobility of the particle. Likewise, aggregation of the nanoparticle due to attractive interactions with Van der Waals forces between nanoparticles leads to prevent the mobility of the nanoparticle in soil. Some of the factors like shape, size, surface area, surface charge, surface coatings, pH and ionic strength are influencing the nanoparticle aggregate formation (Mura et al. 2013). Therefore, soil conditions can enhance or inhibit nanoparticle mobility (Fang et al. 2009). Ben-Moshe (2010) demonstrated that humic acids in soils and aquifers and the ionic strength of resident water can dramatically influence nanoparticle mobility of different types of metal oxides nanoparticles (iron oxide (Fe_3O_4), TiO_2, CuO and ZnO), obtaining the highest mobility for TiO_2 nanoparticles. This may influence the monitoring of nanoparticle composition, fate of soil nutrients, organic pollutants and contaminants.

As like positive effects, negative effects of nanoparticles in soil are also presented by some authors. Nanoparticles like TiO_2, SiO_2 and ZnO are toxic for Gram-positive and Gram-negative bacteria; similarly, silver nanoparticles caused reproductive failure in earthworm *Eisenia foetida* (Heckmann et al. 2011). Negative effects of ZnO nanoparticles were also demonstrated on soil bacterial communities that reduce the microbial biomass and diversity (Ge et al. 2011). Furthermore, soil enzyme activities particularly dehydrogenase activity was decreased when exposed to ZnO nanoparticles. With this treatment, also biomass and root length decreased, showing phytotoxicity due to immobilisation and aggregation of nanoparticles in the soil (Kim et al. 2011; Tripathi et al. 2016).

Even though some of the literatures mentioned about the positive and negative effects of nanoparticles in soil, there is no full-fledged report of biodegradation of nanomaterials in soil and their toxicity in soil ecosystem. So, clear-cut assessment report is needed to understand the nanoparticles mobility, bioavailability, reactivity, ecotoxicity and persistence in soil.

12.8 Conclusion

Plants always thirst for water and crave for food without which plants get starved that leads to vanish the entire human community. So, plant nutrients are essential for plant growth to complete their lifecycle. But widespread soil-nutrient deficiencies in and around the world causes significant lower productivity and quality of crops. External application of nutrient such as fertilisers plays a crucial role on increasing the crop production and productivity. The major problems on this is poor nutrient-use efficiency due to lesser solubility, lower nutrient content of sources, sudden burst of release and not meeting the nutrient demand on growing stages, poor target-based and various means of losses like leaching, runoff, fixation, volatilisation and microbial mineralisation. Hence, the advanced technology, i.e. nanotechnology, can able to puzzle out these problems by developing the slow/smart and controlled release fertiliser that acts like target specific and release the nutrients during the demand-driven period in precise manner. Besides, carbon- and metal oxide-engineered nanoparticles have the potential to enter the root and leaf surface cuticular cells by internalisation process into the plant for better plant metabolic activity. In addition, nanotechnology-enabled nanosensors provide essential information and signals on the optimal times for planting and harvesting crops and the time and level of water, fertilisers, pesticides, herbicides and other treatments along with soil conditions, nutrient status and deficiency of the plants which assist in taking up appropriate and timely corrective measures to reduce the yield loss. Regarding the soil management, nanotechnology-based products like nanosand, nanoclay and nanopolymers for improving the water holding capacity of the soil and iron oxide contain soil clean-up product for removing the heavy metal content in soil and water that are emerging out from the nanotechnology sector. Above all, systematic and thorough quantitative analysis regarding the potential health impacts, environmental clearance and safe disposal of nanomaterials can lead to improvements in designing further applications of nanofertilisers.

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Biosynthesis of Nanoparticles and Their Application in Pharmaceutical Industry

13

Bisma Malik, Tanveer Bilal Pirzadah, Manoj Kumar,
and Reiaz Ul Rehman

Abstract

Nanotechnology originates from the physical, chemical, biological, and engineering sciences where novel approaches are being unfolded to investigate and maneuver single atoms and molecules for multiple applications in different fields of scientific world. In this technology, nanoparticle, a minute object, functions as an entire unit in terms of its transport and attributes. The nanosystem that involves science and engineering technology is one of the most exigent and time-demanding areas of research in nanotechnology. In the recent years, due to the advancement in science and technology, researchers have attempted to synthesize nanoparticles within the size range of 100 nm, and this extensive research and concern on nanoparticles is widening due to their potential application in wide areas of science and technology. The development of technology and progress of mankind have always been connected with the advancements of material science and material processing technology. Currently the research and the progress in nanotechnology and the validation based on various specified size effects in nanomaterials reveal that most of the new findings and designs of the future will be based on qualities of nanomaterials. In this field of technology, nanoparticle has massive scope for pharmaceutical industries which include health-care products and much more such as burn dressings, antimicrobial applications, medical devices, and scaffolds. Several approaches have been employed for the synthesis of nanomaterials which includes chemical reduction, photochemical reactions, electrochemical techniques, and green chemistry route. Among different types of nanoparticles, the metallic nanoparticles such as silver, gold, zinc, iron, and metal oxide have shown considerable improvement in the field of bio-

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medical utilization, not only because of their high surface area-to-volume ratio but also because they display several medicinal properties. It is in this perspective that the current review will focus on the biosynthesis of nanoparticles and their application in pharmaceutical industry and also try to overview the most recent developments in this field.

Keywords
Nanotechnology • Biomedicines • Nanoparticles

13.1 Introduction

The term “nano” is originated from the Greek word “nanos” which means tiny, and it is used as the prefix for one billionth parts (10^{-9}). The American Society for Testing and Materials International (2006) defines nanoparticles as those nanomaterials which have more than two dimensions and are in the range of 1–100 nm in size (Alanazi et al. 2010). These particles have unique and modified physical and chemical properties because of their particular electronic structure; large reactive, open surface area; and quantum size effects. A nanoparticle nowadays finds its application in many research areas such as biomedicine, electronics, cosmetics, textiles, etc. (Guglielmo et al. 2010; Prasad et al. 2014). It has been found that due to expeditious industrialization and urbanization, an extensive amount of dangerous and unsafe chemicals, gases, or substances are liberated into the environment, thus degrading its quality, and now it is the need of the hour to unravel the secrets of the nature and its by-products which results in the development of the nanoparticle synthesis process. It is noteworthy to mention that the application of nanotechnology is highly convenient to biological samples due to their intensive properties. These biological samples undergo extremely controlled assembly for making them convenient for the synthesis of metal nanoparticles which is found to be trustworthy and eco-friendly (Harekrishna et al. 2009; Prasad 2014; Prasad et al. 2016). In addition to this, the process of synthesis of semiconductor nanoparticles is becoming an upcoming area of research due to its exclusive applications in various fields which lead in the developmental growth of novel. Besides, nanotechnology as a field of research opens new insights in research field specifically in the field of material science. This is because the nanoparticle exhibits highly new or modified properties which include its shape, size, distribution, and external features of the particles. That is why the nanoparticles or nanomaterials find its application in almost every field and emerge as one of the active research areas in modern material science (Kaviya et al. 2011). Nanotechnology as a field of research is progressing day by day, creating an impact in almost every sphere of human lives and generating a growing excitement in the biological science field particularly biotechnology and biomedical science (Prashanth et al. 2011). As nanoparticles show improved properties on specific attributes such as distribution, size, and shape, nanocrystalline particles have found immense applications in the field of high-sensitivity biomolecular detection and diagnostics, therapeutics and antimicrobials (Sridhara et al. 2012), catalysis, and microelectronics (Veera et al. 2012). Besides these extraordinary applications of nanoparticles, there is a need of the hour to find out the clean routes (biological route) for the synthesis of nanoparticles which are commercially viable and eco-friendly in nature (Lekshmi et al. 2012). To address this concern, a number of approaches are available, for example, solution reduction; photochemical and chemical reactions; thermal decomposition of nanoparticle compounds (Akl et al. 2012); electrochemical, radiation-assisted, microwave-assisted process; and currently the use of biological samples (green chemistry) (Ravindra et al. 2012) for the synthesis of nanoparticles. Due to certain limitations and ill effects of chemical synthesis of nanoparticles, the utilization of environmentally benign material like plant extract (leave, flower, bark, seed, peels, etc.), fungi, bacteria, and enzyme for the synthesis of nanoparticles provides various advantages like eco-friendliness and compatibility for biomedical and other pharmaceutical applications as these synthesis procedures do not utilize any toxic chemicals (Gokulakrishnan et al. 2012). Various synthesis procedures (green chemistry route) have been already started for the synthesis of metal nanoparticles such as the use of fungi like *Fusarium oxysporum* (Nelson et al. 2005), *Penicillium* sp. (Hemanth et al. 2010), and bacteria such as *Bacillus subtilis*, (Elumalai et al. 2010). In addition to this, nanoparticle synthesis by employing plant sources or extracts is the highly accepted approach of green, environment-friendly production of nanoparticles as it exhibited a unique advantage, that is, the plants are widely distributed and readily available, are much secure to deal with, and also act as a factory of various important metabolites (Ankamwar et al. 2005). Hence synthesis of nanoparticles through green chemistry route holds a great promise not only in terms of multiple applications in diverse fields of science but also for the healthy environment. As far as nanoparticle applications are concerned, it has been long identified that these are having inhibitory effects on microbes present in industrial and medical processes (Nasrollahi et al. 2011). Nanoparticles nowadays find its application in every important field of science which includes the high sensitive areas like genomics, immune modulation, biosensors, clinical chemistry, control of microorganism, and diagnostic procedures (detection and targeted drug delivery) (Diva et al. 2012). Furthermore, these biosynthesized nanoparticles were found to be extremely toxic against various multidrug-resistant human pathogens. Besides this, the work is in progress to answer the questions that limit the biosynthesis and application of nanoparticles to diverse systems in one way or the other. There are different types of nanoparticles, but the metallic nanoparticles such as gold, silver, zinc, iron, and metal oxide nanoparticles proved to be of great importance in biomedical application not only because of their large surface area-to-volume ratio (Bhattacharya and Mukherjee 2008; Prasad et al. 2016) but also because of their unique properties that show multifunctional aspect of these particles in diverse fields (Fig. 13.1) (Hussain and Ferguson 2006).

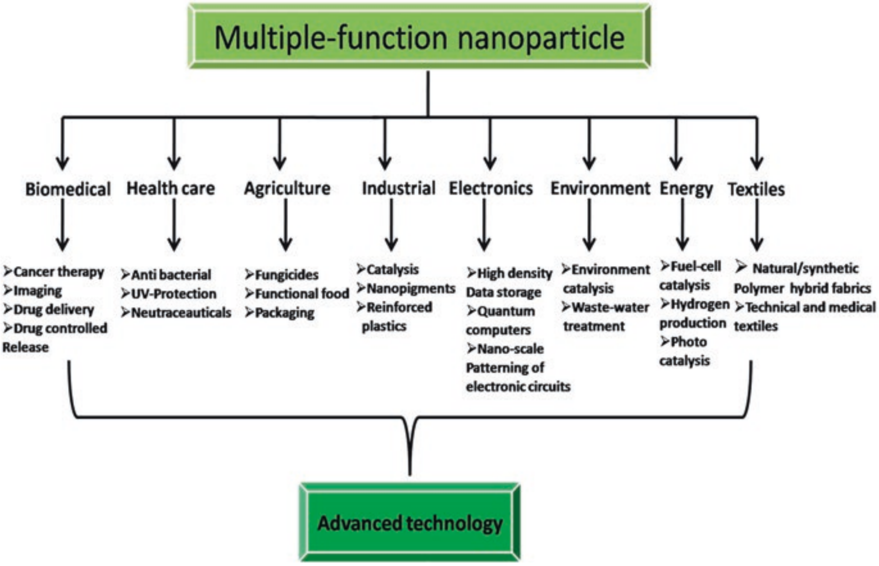

Fig. 13.1 Advanced functions of metal nanoparticle in multiple fields

13.2 Why Green Synthesis?

Green synthesis provides various advantages over physical and chemical method of nanoparticle synthesis as it is a cost-effective, eco-friendly, easy modification procedure for high-scale production of nanoparticles as this method of synthesis does not use any hazardous chemicals, high pressure, temperature, and high amount of energy (Fig.13.2) (Ravindra et al. 2012; Prasad 2014).

13.2.1 The Green Route for Biosynthesis of Nanoparticles

Several different procedures for the synthesis of nano- and microscale nanomaterials which contributes to the advancement of relatively novel and highly unexplored area of research depend upon the procedures of biosynthesis of nanomaterials (Salam et al. 2012).It is very important to mention that the biosynthesis of nanoparticles should be cost-effective and eco-friendly so that the synthesis and the applications do not remain restrict to one or other areas of research. The best way of synthesizing of nanoparticle is through green chemistry route that makes use of eco-friendly, nontoxic, and safe reagent (Prasad 2014). There are different methods of extracting a metal from its source that depends upon the type of protocol followed. The term "phytomining" refers to the uses of hyperaccumulating plants to extract a metal from the biomass to return an economic profit (Lamb et al. 2001). Hyperaccumulation species have a physiological mechanism that regulates the soil solution concentration of metals. Mechanism of biosynthesis of nanoparticles in

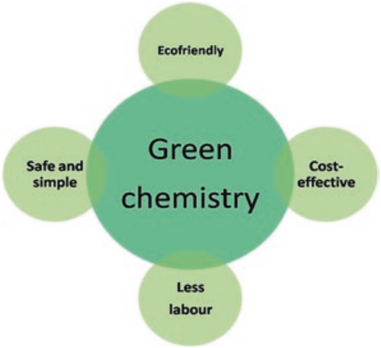

Fig. 13.2 Advantages of green synthesis

plants may be in association with phytoremediation concept in plants (Haverkamp et al. 2007).

Biological Method Extract from biological organisms may act both as reducing and capping agent in the synthesis process of nanoparticles. In the biological method of synthesis, the reduction of metal ions takes place by the combination of biomolecules found in these extracts such as protein/enzymes, polysaccharide, vitamins, and amino acids that are environmentally benign but yet are chemically complex and diverse. Several studies have reported the successful synthesis of nanomaterials by using bioorganic compounds (Sahayaraj and Rajesh 2011). Perhaps, the biological methods are termed as safer, cost-effective, eco-friendly, and sustainable procedure for the synthesis of nanoparticles yet much more is still unanswered (Diva et al. 2012). Currently, biological method for the synthesis of nanoparticles is progressing day by day and becomes the thrust area of research due to its sustainable and eco-friendly nature; though the nanoparticle biosynthesis by plants such as alfalfa, *Emblica officinalis*, lemon grass, *Aloe vera*, *Tamarindus indica*, and *Cinnamomum camphora* has been described, the benefits of these plants as biological materials for the nanoparticle synthesis are yet to be unexplored (Yogeswari et al. 2012). Biosynthesis of nanoparticles with their shape, size, natural resources, and plant part used is given in Table 13.1 A generalized scheme of nanoparticle synthesis by using biological materials is given in Fig. 13.3.

13.3 Biosynthesis of Nanoparticles: Overview and Applications

Green synthetic approach of nanoparticles is more advantageous over the chemical approach because of its simple, cost-effective, and eco-friendly nature. Biosynthesis of nanoparticles can be categorized into organic, inorganic, and hybrid. Among the biosynthetic approach of nanoparticles, most of macromolecules and cellular substructures are able to form NPs based on environmental conditions and sample treatment. Green synthesis of nanoparticles has already been reported using many living

Table 13.1 Biosynthesis of nanoparticles with their size, shape, and plant parts used

S. No.	Nano particles (NPs)	Natural resource	Part used	Component	Size (nm)	Shape
1.	Ag	*Ocimum sanctum*	Leaves	$AgNO_3$	20	Spherical
2.	Ag	*Allium cepa*	Onion (bulb)	$AgNO_3$	33.6	Spherical
3.	Ag	*Costus speciosus*	Callus culture	$AgNO_3$	420	Spherical
4.	Ag	*Oryza sativa*, *Vigna radiata*, *Brassica campestris*	Seeds	$AgNO_3$	25	Spherical
5.	Ag	*Tridax procumbens*	Leaves	$AgNO_3$	55	–
6.	Ag	*Euphorbia hitra*	Leaves	$AgNO_3$	50	Spherical
7.	Ag	*Ficus benghalensis*	Leaves	$AgNO_3$	44	Spherical
8.	Ag	*Svensonia hyderobadensis*, *Boswellia ovalifoliolata*, *Shorea tumbuggaia*	Leaves, Bark	$AgNO_3$	430	–
9.	Ag	*Withania somnifera*	Leaves	$AgNO_3$	40	Spherical
10.	Ag	*Ocimum sanctum*	Leaves	$AgNO_3$	50	–
11.	Ag	*Ocimum sanctum*	Leaves	$AgNO_3$	30	Spherical
12.	Ag	*Euphorbia prostrata*	Leaves	$AgNO_3$	80	Rod
13.	Ag	*Trianthema decandra*	Roots	$AgNO_3$	50	Hexagonal
14.	Ag	Mulberry	Leaves	$AgNO_3$	40	Spherical
15.	Ag	*Cassia auriculata*	Leaves	$AgNO_3$	–	Spherical
16.	Ag	*Solanum xanthocarpum*	Berry	$AgNO_3$	406	Spherical
17.	Ag	*Vitex negundo*	Leaves	$AgNO_3$	30	Spherical
18.	Ag	*Elaeognus latifolia*	Leaves	$AgNO_3$	50	Spherical
19.	Ag	*Azadirachta indica*, Triphala	Leaves, Powder	$AgNO_3$	59	Spherical
20.	Ag	*Cleome viscosa*	Leaves	$AgNO_3$	50	Spherical
21.	Ag	*Saururus chinenis*	Leaves	$AgNO_3$	54	Spherical
22.	Ag	*Ocimum basilicum*	Leaves	$AgNO_3$	89	Spherical
23.	Ag, Au	*Memecylon umbellatum*	Leaves	$AgNO_3$, $HAuCl_4$	20	Spherical
24.	Ag, Au	*Punica granatum*	Peels	AgNO3, $HAuCl_4$	25	Spherical
25.	CdO	*Achillea wilhelmsii*	Flowers	$CdCl_2$	10, 35	Spherical
26.	ZnO	*Calotropis procera*	Milky latex	$\{(CH_3CO)_2 Zn_2.H_2O\}$	40	Spherical
27.	Ag	*Punica granatum*	Seeds	$AgNO_3$	400	Spherical
28.	Ag	*Punica granatum*, *Rosa damascena*	Peels, Petals	$AgNO_3$	21	Spherical

(continued)

Table 13.1 (continued)

S. No.	Nano particles (NPs)	Natural resource	Part used	Component	Size (nm)	Shape
29.	Ag	*Punica granatum*	Seeds	$AgNO_3$	20	Spherical
30.	Ag	Loquat	Leaves	$AgNO_3$	18	Spherical
31.	Cr_2O_3	*Arachis hypogaea*	Leaves	K_2CrO4	80	Hexagonal
32.	Au	*Putranjiva roxburghii*	Leaves	$HAuCl_4$	38	Spherical
33.	Au	*Caesalpinia pulcherrima*	Flowers	$HAuCl_4$	50	Spherical
34.	Ag	*Nerium oleander*	Leaves	$AgNO_3$	67	–
35.	Au	*Tagetes erecta*	Flowers	$HAuCl_4$	10	Spherical
36.	Au	*Allium cepa*	Bulb	$HAuCl_4$	54	Spherical

organisms ranging from yeast, fungi, plants, and algae to bacteria (eubacteria, cyanobacteria), as recently reviewed (Durán et al. 2007, 2011; Mohanpuria et al. 2008; Narayanan and Sakthivel 2010, 2011; Rodriguez-Carmona and Villaverde 2010; Lloyd et al. 2011; Durán and Marcato 2012; Prasad et al. 2016). Green nanoparticles can be synthesized from carbohydrates, lipids, DNA, proteins, and also complex molecular mixtures. After cell lysis, sample treatments could involve many strategies commonly used for cell fractioning including solvents, salts, homogenization in the presence of surfactants, chaotropic agents, and differential precipitation. However, inorganic bioNPs can be classified into oxides and metallic. The synthesis of inorganic bioNPs is carried out by unspecific reducing agents present in the medium and/or as the result of triggering the SOS system in the cell to reduce toxicity. In the case of hybrid bioNPs, the synthesis can be driven by molecular precursors in the presence of biological templates (e.g., DNA, proteins) (Contescu and Putyera 2009). The advantage of using biological templates is the huge diversity of tridimensional biostructures available as templates that can be used to create NPs with many different characteristics and properties. Two main strategies were developed for bioNPs production: either by using biological extracts or specific molecules, named as in vitro biosynthesis, or using living cells, named as in vivo biosynthesis.

13.3.1 Silver Nanoparticles

Silver nanoparticles have attracted intensive research interest because of their immense potential as antimicrobial, photocatalytic agents, and surface-enhanced Raman scattering (Gokulakrishnan et al. 2012; Aziz et al. 2015, 2016). Apart from physiochemical methods, AgNPs can also be synthesized using a green approach, i.e., reduction of aqueous Ag ions with the culture supernatants of *Staphylococcus aureus* (Nanda and Saravanan 2009). Biosynthesis of AgNPs involves the use of microbial or plant extract that acts as a reducing agent and reduces Ag^{2+} to Ag^0, and the spectra are measured by UV-Vis spectrophotometer at a resolution of 1 nm.

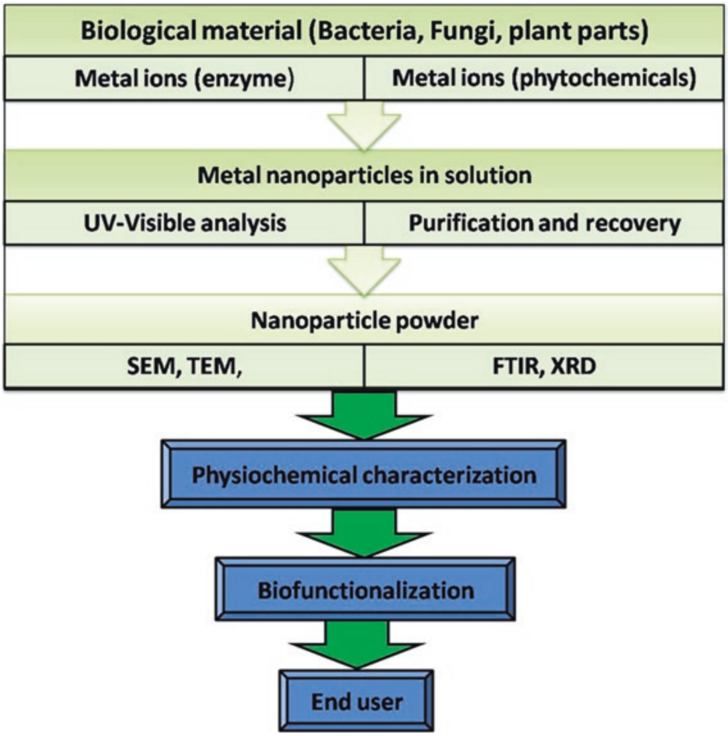

Fig. 13.3 Flowchart of biological synthesis of nanoparticles

Shahverdi et al. (2007) reported the use of fungus *Alternaria alternata* to produce AgNPs. Several hypotheses explain the antimicrobial activity of silver nanoparticles such as rapid breakdown of silver nanoparticles releases ionic silver that inactivates vital bacterial enzymes by interacting with essential -SH groups. Ag ions can also inhibit bacterial DNA replication, damage bacterial cytoplasm membranes, deplete levels of intracellular adenosine triphosphate (ATP), and finally cause apoptosis (Parveen et al. 2012; Aziz et al. 2015). Silver has a very long history in the medical sector as it was used to treat many ailments such as epilepsy, venereal infections, acnes, and leg ulcers. Besides, silver foil was applied to surgical wounds for improved healing and reduced postoperative infections, while silver and lunar caustic (pencil containing silver nitrate mitigated with potassium nitrate) was used for wart removal and ulcer debridement (Klasen 2000). Perhaps the most well-documented and commonly used application of silver nanoparticles for this is the use of wound dressings (Leaper 2006). Sibbald et al. (2007) reported that silver nanoparticle dressing has a potential effect of protecting the wound site from bacterial contamination. Besides, medicine sector Ag-NP finds immense potential in cosmetics sector because of its antimicrobial as well as soothing effect (Aziz et al. 2016). The high surface area-to-volume ratio of silver nanoparticles increases their contact with microorganisms, promoting the dissolution of silver ions, thereby improving biocidal effectiveness. Dhrutika et al. (2013) reported that the ability of the AgNPs to release Ag^{3+} is a key to their antimicrobial activity. Some antimicrobial activities of agent are extremely toxic and irritant, and much interest in finding ways to formulate novel types of safe and cost-effective biocidal materials is the need of the hour (Dhrutika et al. 2013). Chemical synthesis of AgNPs involves the commonly used borohydrides and other stabilizing chemicals that act as capping agents bind to the nanoparticle surface and improve stability and water solubility, which are essential to prevent aggregation; examples include water-soluble polymers, oligosaccharides and polysaccharides, sodium dodecyl sulfate, and glycolipid (Sondi and Sondi 2004). Chemosynthetic approach of AgNPs possesses some drawbacks such as extremely expensive use of certain toxic substances, thus posing various ill effects to the environment.

13.3.2 Gold Nanoparticles

Nanoparticles are extensively and particularly exploited in microorganism because of their biocompatibility; gold nanoparticles are considered to be biologically intent but can be engineered to possess photochemical and chemical functionality (Prasson and Chittaranjan 2012). Depending upon the physical properties (size, shape, etc.), gold nanoparticles are categorized into various subtypes like gold nano-cages, nanospheres, nano-needles, and nanorods with characteristics near infrared irradiation absorption which can destroy cancer cells and bacteria via photothermal heating (Hasna et al. 2012). Among these subtypes, nanospheres are the earliest studied nanoparticles that are synthesized under controlled reduction of aqueous $HAuCl_4$ solution by using different reducing agents like citric acid that possesses the ability to generate monodisperse gold nanospheres (Turkevich et al. 1951; Frens 1973). However, the size of these nanospheres can be regulated by varying concentration of citric acid/gold ratio. Usually little amount of citric acid results in the formation of nanospheres with larger size; besides, another important drawback of this protocol is the low yield and the restriction of using water as the solvent. Faraday (1857) proposed a two-phase system that has the capability of producing thermally and air-stable gold nanospheres with reduced disparity and controlled size (10 nm) as reported in 1993 (Giersig and Mulvaney 1993). Later this technique was also improved by using phase-transfer reagents, viz., tetra octyl ammonium bromide (Brust et al. 1994), but the physical properties (size) still rely on the ratio of reducing agent and gold concentration. Later, researchers also investigated other protocols for the synthesis of gold nanospheres by using several reductant or ligands (Leff et al. 1996; Weare et al. 2000; Hiramatsu and Osterloh 2004). Several reports reveal the use of dendrimers as templates or stabilizers for gold nanosphere synthesis (Esumi et al. 1998; Garcia et al. 1999; Manna et al. 2001; Kim et al. 2004; Scott et al. 2005; Shi et al. 2006, 2008). Another gold nanoparticle subtype is the nanorods, which are synthesized by using numerous strategies, such as template method that is based on electrochemical deposition of gold salt within the pores of nanoporous polycarbonate or alumina template membranes (Martin 1994; Reetz and Helbig

1994; Yu et al. 1997; van der Zande et al. 1997; Chang et al. 1999).However, the seed-mediated synthesis of gold nanorods is a well-established protocol that has gained wide importance as compared to other protocols (Jana et al. 2001b; Busbee et al. 2003). Jana et al. (2001a, 2002) reported that gold nanorods can be synthesized in a quantitative yield when silver nitrate is added to it. In addition to above-mentioned methods, numerous other strategies have also been investigated especially for the fabrication of gold nanorods that includes bio-reduction (Canizal et al. 2001), growth on mica surface (Mieszawska and Zamborini 2005), and photochemical synthesis (Kim et al. 2002). Gold nanoparticles can be combined with photosensitizers for photodynamic antimicrobial chemotherapy; gold nanoparticles conjugated with photosensitizers can kill methicillin-resistant *Staphylococcus aureus* (MRSA) by photodynamic antimicrobial chemotherapy and NIR photothermal radiation (Tikariha et al. 2012). Gold nanoparticles have been successfully synthesized using various fungi and bacteria. Gold nanoparticles with antibodies and antibiotics also have been used for selective photothermal killing of bacteria and protozoa.

13.3.3 Zinc Oxide Nanoparticles

Green synthesis of spherical-shaped zinc nanoparticles was first carried out by using milky latex of *Calotropis procera* that acts as reducing as well as stabilizing agent. Ravindra et al. (2012) carried out biosynthesis of zinc oxide nanoparticles by using *Aloe vera* extract, and later these nanoparticles were characterized by means of various standard techniques. The precipitation method was used followed by controlled and freezing-drying processes, and the material obtained was thermally treated at various temperatures, and the influence of temperature or textural, morphological, and structural properties of the material can be studied by the techniques of scanning electron microscopy, transmission electron microscopy, thermal analysis, etc. (Haritha et al. 2011). Zinc nanoparticles find great application in the pharmaceutical sector as they emerges as novel antimicrobial agents (Bhuyan et al. 2015) because of high surface area-to-volume ratio. In the recent year, the interest in nanoparticles increases due to the growing microbial resistances against metal ions, antibiotic development of resistant strains, etc. (Haritha et al. 2011). Currently, zinc oxide nanoparticles are being used in the field of porous and nanometric materials prepared by nonconventional processes. Besides, these are also used in solar cells, ceramics, catalysts, cosmetic, and gas sensors (Dhrutika et al. 2013).

13.3.4 Copper Oxide Nanoparticles

Green synthesis of copper oxide nanoparticles using antimicrobial activity is an important area of research in bio-nanotechnology. This is an emerging cost-effective, eco-friendly science of well-defined shape and size and controlled monodispersity. One of the recent studies carried out by the researchers proposed biosynthesis of extraneous production of copper oxide nanoparticles. Soheyla et al. (2012) reported that copper nanoparticles are synthesized and stabilized by using *Penicillium aurantiogriseum*, *Penicillium citrinum*, and *Penicillium waksmanii* isolated from the soil. Copper nanoparticles can easily oxidize to form copper oxide. The copper nanoparticles can be protected from oxidation, generally by encapsulating the copper nanoparticle in organic or inorganic material such as carbon and silica (Abdul et al. 2009).The various biological reducing agents used in the synthesis of copper nanoparticles are bacteria, actinomycetes, fungi, yeast, and plants. Green synthesis of nanoparticles employed the use of different microorganisms to produce inorganic materials, either intracellularly or extracellularly with the properties that are similar to biological and chemical materials (Amrut et al. 2010). Although synthesis of nanoparticles using biological agents has not been devised yet, some studies suggested that different biomolecules are responsible for the synthesis of copper nanoparticles. But in the intracellular and extracellular biosynthesis of nanoparticles by fungi, numerous capping and reducing agents are employed that possibly involved also effects of the shape and size of these nanoparticles which need to be clarified (Shloma et al. 2010).

13.3.5 Titanium Dioxide Nanoparticles

Green synthesis of nanoparticles currently has immense potential in various sectors because of environment-friendly nature and cost-effectiveness. Synthesis of nanoparticles depends upon numerous parameters such as size, shape, morphology, nature, and composition of the material used. TiO_2 finds great application in water and air purification system because of their potential oxidation strength, high photostability, and nontoxic nature. Besides, these nanoparticles possess other unique features like optical and chemical stability and catalytic activity, therefore possessing immense industrial applications like photocatalysts and in pigments (Parthasarathi and Thilagavathi 2009). However, green synthesis of nanoparticles depends on various factors such as choice of the solvent, reducing and stabilizing agent. Currently, the biosynthesis of nanoparticles was achieved by microorganisms like bacteria and actinomycetes. In addition to this, leaf extract of *Nyctanthes* was used to synthesize TiO_2 nanoparticles because of its antinociceptive, antioxidant, anti-inflammatory, antidiabetic, antifungal, and antimicrobial activity. The biosynthesis of nanoparticles has not been yet extended for the synthesis of titanium dioxide nanoparticles especially with Nyctanthes (Sundrarajan and Gowri 2011).

13.4 Nanoparticles: The Real "Metal Bullets" in Clinical Medicines

Nowadays nanoparticles possess immense potential especially in the medical sector and can be used as antimicrobicides. Moreover, nanoparticles show sharp prejudice from their bulk in many respects which becomes bonus for developing diagnostic

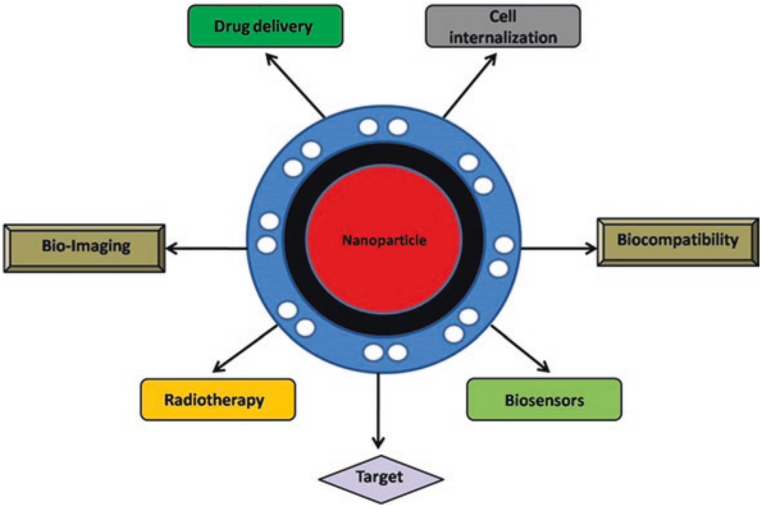

Fig. 13.4 Multiple functions of nanoparticle in clinical medicines

tools and antimicrobials (Ravindra et al. 2012).Moreover, they play a pivotal role in drug delivery system and are also used as hyperthermic agents because they act as mediators of drug release (Khlebtsov and Dykman 2010; Prasad et al. 2017). The various functions of metal nanoparticles particularly to clinical medicines are shown in Fig. 13.4. Due to certain unique properties of nanoparticles such as small size (1–100 nm), large surface area-to-volume ratio, greater affinity toward target candidate, and other special features, these act as potential probes of biological markers (Sahayaraj and Rajesh 2011; Jain and Aggarwal 2012). Presently, the main focus of the scientists is to control the structural dynamics (e.g., size and shape) of these nanoparticles because it has a great influence on its properties (catalytic, magnetic, as well as optical). Due to the nano-size of these particles, they possess immense potential in tumor diagnosis and treatment (Cai and Chen 2007).The most well-studied nanoparticles include quantum dots (Cai et al. 2006, 2007), carbon nanotubes (Liu et al. 2007), paramagnetic nanoparticles (Thorek et al. 2006), liposomes (Park et al. 2004), gold nanoparticles (Huang et al. 2007), and many others (Ferrari 2005; Grodzinski et al. 2006). Besides, these nanoparticles especially metal oxides possess a significant role in biomedical sensors, fabrication, fuel cells, and other medical gadgets (Chen et al. 1998; Prasad et al. 2014). Among inorganic materials, oxides like ZnO, MgO, CaO, and TiO_2 are of particular interest because their stability is maintained even in harsh conditions and are generally regarded as safe materials to organisms (Stoimenov et al. 2002; Fu et al. 2005). Nanoparticles especially silver and zinc act as potential antitopical agents to cure infectious diseases due to antimicrobial properties (Dickson and Lyon 2000). These metal oxides possess a strong inhibitory and bactericidal effects against fungi, virus, and bacteria; that is why they have been used since ancient times to cure infection and burns (Saha et al. 2011). In medical sector due to continuous use of spurious and over-the-counter drugs, the resistance of microorganisms against antibiotics has been increased (Nithya and Ragunathan 2009).Therefore, developing novel, cost-effective, and safe drug formulations is the need of the hour to cure such type of infectious diseases (Hasna et al. 2012). Aziz et al. (2016) evaluated various antimicrobial activities of silver nanoparticles against different microorganisms. This property is considered as most exploited nature of nanoparticles in the medical field. Oza et al. (2012) describes the use of these nanoparticles in the formulation of dental resins and ion exchange fibers and in coating of medical equipment. Moreover, these metal nanoparticles show photoelectric effect which neutralizes the photobleaching concerns related with the conventional fluorescent dyes.

13.5 Summary and Outlook

Nanotechnology in the current scenario is a revolutionary field, and its advancement enabled us to utilize particles in the size of nanoscale. This is the beginning in the field of nanosystems, the trend in the next decade being its integration with the green chemistry route. This field comprises of several strategies that involve extensive strain selection, cultivation modes, recombinant DNA technology, metabolic engineering, protein designing and reengineering, and predictive modeling which allow us to create nanobioreactors resulting in the creation of a new nanobiotechnology arena exhibiting high potential impact in several fields. The application of nanomaterials has created new therapeutic horizons, and in case of nanoparticles (silver, gold), the current data reveals only the surface of the potential benefits and the wide range of applications. The nanoparticle system presently approved in many cases increased the therapeutic index of drugs by decreasing the drug toxicity or elevating the efficacy by targeting ligands such as antibodies, pesticides, and aptamers which may further improve the therapeutic nanoparticle system in the next generations. Multifunctionality of nanoparticles becomes more complex system as they are capable of targeting imaging and therapy which may be the subject of the future research. As the functionality of nanoparticles becomes more complex, there is a trend to redesign the nanoparticles with optimally physiochemical and biological properties to achieve the desired function. Indeed, this was the biggest hindrance for the nanoparticles to enter the clinical practices, with the fact that many targeted liposome was described more than 20 years ago, but none have been ever approved for use. With the introduction of safer nanoparticles together with novel emerging approaches, we except the more number of multifunctional nanomaterials enter into the clinical practices in the near future. As far as synthesis of nanoparticles is considered, the green chemistry approach is of great importance due to eco-friendly and cost-effective approach with wide range of applications such as in nanomedicines, catalysis medicines, nano-optoelectronics, and many more. This new and emerging field of research in the current scenario with day by day developments holds a good promise for the bright future in this field. This green chemistry route involves the synthesis of nanoparticles that have several advantages including the ease of the scaled-up processes, economic viability, etc. It was concluded that the plant-based synthesis of nanoparticles like silver and gold possesses potential clinical benefits and the nanoparticle so obtained in nano-dimensions would be equally effective in medicinal applications as that of antibiotics and several other drugs. The application of these plant-mediated nanoparticles in drug delivery system might be the thrust area of research in nanomedicines. This green chemistry route for the synthesis of nanoparticles includes bacteria, yeast, fungi, several plant biomass, or plant extracts which have tremendous application in biology with continued research and developmental efforts; nanotechnology is expected to have a tremendous impact on medicines for decades to come. The ongoing research was focused on the safety measures of nanomaterials, which is a critical point to be addressed for further development in the advancement of technology. There are many challenges ahead that need to be addressed and solved in order to make nanoparticle-based products commercially viable. Now, the need of the hour is to develop the cost-effective procedures for producing reproducible, biocompatible, and stable nanoparticles from bioresources.

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Nanomaterials Act as Plant Defense Mechanism

14

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Abstract

Plants symbolize the prevalent edge between the environment and biosphere, so discovering how nanomaterials affect them is particularly significant for ecological assessments. Metal-based nanoparticles (NPs) can cause toxicity to terrestrial plants; however, there is little understanding of plant defense mechanisms that may counteract nanotoxicity. The occurrence of oxidative pressure is one of the major biochemical alterations following nanoparticle exposure, and it changes the balance between cell function and antioxidative defense mechanisms. Biochemical aspects generally cause the production of excess reactive oxygen species (ROS), disturbing membrane transport mechanisms, oxidative harm to the cell membrane, and DNA degradation. Globally plants had developed the antioxidant mechanism which tends to eliminate the access manufacture of ROS i.e. H_2O_2, OH^- and O_2 free radicals. Improved levels of antioxidative enzymes, for instance, superoxide dismutase (SOD), catalase (CAT), and peroxidase (POX), are able to support plant cells in lightening the oxidative stress induced by different nanostructures. As the vital signals resolving defense gene establishment, ROS are principally drawn in the initiation of plant disease resistance responses. Further reviews are still needed to understand plant defense mechanism against the potential hazards of nanomaterials.

Keywords

Nanomaterials • Plant defense mechanism • Cerium oxide • Chitosan • Silicon

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14.1 Introduction

Nanomaterials are particles having a minimum of one dimension smaller than 100 nm. These particles are of great interest because they can bridge the gap among bulk materials and atomic molecular makeup. This is incredibly interesting from scientific point of view, because as it gets smaller, it starts changing its properties (Kothandapani and Mishra 2013). Nanoparticles such as zinc oxide, titanium dioxide have ability to block sun rays and therefore used in preparation of sun block creams and lotions. The use of the word "nano" allows researchers to draw attention to the facts regarding material structures, design, and optimized use of vague properties and behaviors by length from 10^{-7} to 10^{-9} m (Ozimek et al. 2010). The potential advantages of nanomaterials have been recognized by many industries and many commercial products are manufactured such as food, aerospace, pharmaceutical, microelectronics and cosmetic industries (Saboktakin 2012). Progresses in these commercial enterprises are propelled by basic and functional research in physics, chemistry, biology, engineering, and material sciences. Achievements and discoveries of nanosciences in food and linked industries are restricted. The structural orientation of compound at nanoscale is significantly dissimilar to the macroscopic counterparts with respect to physical, chemical and biological properties. Nanomaterial research is presently a part of passionate scientific significance due to the diversity of promising application in biomedical, optical, and electronic fields (Prasad et al. 2014). The national nanoscience program has led to liberal public grant for nanoscience research in the USA (Suganeswari et al. 2011). Numerous nanoparticles are manufactured possessing applications in designing and development of optical devices, sensor technology, catalyst, bactericide, electronics, biological labeling, treatment of cancer, and many more (Prasad et al. 2016, 2017). In previous decade, application of nanomaterials has been extensively increased, and high demands lead to the bulk production of the nanomaterials. Classically nanomaterials are produced by physical and chemical methods, as these methods are very expensive, poisonous, and non-eco-friendly. In current scenario, scientists are looking for the alternative methods, i.e., biological methods which are low cost, non-toxic, and eco-friendly (Prasad 2014; Prasad et al. 2016).

NPs are source for various biological and chemical effects on terrestrial plants. (Du et al. 2016). Numerous studies have demonstrated the metal nanoparticle's phytotoxicity caused by the manufacture of reactive oxygen species (ROS), which subsequently results in oxidative stress, lipid peroxidation, and protein and DNA damage in plants (Arruda et al. 2015; Ma et al. 2015a; Tripathi et al. 2017a, b; Singh et al. 2017a, b).

Plant cells cannot move so each cell is needed to be capable of defending themselves from the attack of stress and pathogens. Only proteins are involved in plant defense responses and proper cell functioning. Plants had evolved the two types of well defense mechanism. The first line of defense takes place when plant cells sense the presence of herbivore (by detecting general characteristics like flagella of bacteria or the chitin in fungi cell walls) and alert nearby cells by secreting certain chemical molecules that alert other surrounding cells to amplify their defense reaction (Freeman and Beattie 2008). For example, in response to harmful pathogens or invaders, the alerted plant cells may secrete certain molecules that build extra walls for protection. Pathogens evolved and developed the mechanism to tackle the plant first line of defense, in response plant evolved and developed second line of defense. The second line of defense protects the plant from invaders. There are diverse indicators that help to indicate which type of defense must be activated in plant in response to what type of pathogen. By analyzing these signs and the genome of plants, scientists can find out which parts of the plant genome and which proteins are implemented in defense system. The example of the activation of secondary defense response is hypersensitive response (HR). Plant cells align around the pathogen attack site and kill themselves to restrict pathogen from dispersion throughout the plant. This inhibits pathogen uptake of water and nutrients from plants.

14.2 Nanoparticles Exhibiting Plant Defense Mechanisms

Nanoparticles are the interesting topic for research because their property at nanoscale is different as compared to its normal size. Nanomaterials have been used in crop growing to improve seed germination and plant development and to guard crops from biotic stresses, i.e., herbivore (Khodakovskaya et al. 2009). However, the unique properties of NPs on living organisms in the ecosystem may experience oxidative stress induced by NPs (Majumdar et al. 2014). Plants can activate various enzymatic and nonenzymatic defense systems (Rico et al. 2015) against stress. One of the interesting properties is amplification of defense response in plants through nanoparticles (Table 14.1). Chitosan is known to possess antifungal properties against plant pathogens and induce disease resistance. TiO_2 increases the enzyme activities which decreases the accumulation of reactive oxygen species. Silicon nanoparticles are known to enhance the fungal resistance in maize by expressing higher level of phenolic compound and lower level of stress-responsive enzymes against fungi. A combination of *Pseudomonas fluorescens* and silica NPs in soil increases phenolic action and trims down the stress by the inhibition of responsive enzymes in maize. This elevated level of phenolics is established to induce silica accumulation in leaf epidermal layer, thereby conferring a defensive physical wall as well as induced disease resistance (Rangaraj et al. 2014). Copper oxide nanoparticles accumulate in the plant cells and increase the significant levels of superoxide dismutase, catalase, and lipid peroxidase.

A large number of reports have studied activation of antioxidative enzymes in response to nanomaterial exposure (Tripathi et al. 2017a, c). Antioxidant enzymes can be activated by a variety of nanomaterials i.e. $n\mathrm{CeO_2}$, $n\mathrm{Fe_3O_4}$, and $n\mathrm{Co_3O_4}$ can induce CAT; $n\mathrm{CeO_2}$, $n\mathrm{Fe_3O_4}$, $n\mathrm{Co_3O_4}$, $n\mathrm{MnO_2}$, $n\mathrm{CuO}$, and $n\mathrm{Au}$ can induce GPX; and $n\mathrm{CeO_2}$, $n\mathrm{Pt}$, and fullerene can induce SOD (Tripathi et al. 2016a). Antioxidant defense mechanism of plants employs both enzymatic agents such as superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX), guaiacol peroxidase (GPX), dehydroascorbatereductase (DHAR), and glutathione reductase (GR)

Table 14.1 Nanoparticles and its mode of action

S. no	Nanoparticles	Mode of action	References
1	Chitosan	Upregulation of defense-related genes including that of several antioxidant enzymes as well as Elevation of the levels of total phenolics and NO signaling molecule	Chandra et al. (2015)
2	TiO_2	Increased activity of superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD) and decreased accumulation of reactive oxygen free radicals	Hong et al. (2005)
3	Multi-walled carbon nanotubes (MWCNTs)	Activation of ROS defense response cascade, which is sufficient to prevent microbial pathogens from completing their life cycle Generation of ROS such as super peroxides and H_2O_2	Tan et al. (2009) and Begum and Fugetsu (2012)
4	Silicon	Enhanced fungal resistance in maize	Rangaraj et al. (2014)
5	Copper oxide	Increases levels of SOD, CAT, and lipid peroxidase	Nekrasova et al. 2011
6	Cerium oxide	CeO_2 concentration-dependent induction of lipid peroxidation and photosynthetic stress in rice seedlings (modifications of antioxidant defense system)	Majumdar et al. (2014)
7	Zinc oxide	Increased GSH levels and CAT activity	Zhao et al. (2013)

and nonenzymatic antioxidants such as ascorbate, glutathione, thiols, phenolics, etc. (Singh et al. 2015; Rico et al. 2015). ROS are fairly manufactured as by-products of metabolic pathways in chloroplasts and are also accountable for chlorophyll degradation (Melegari et al. 2013; Rico et al. 2015; Ma et al. 2015a; Singh et al. 2017a, b). However, disorder in plant photosynthetic activity by NPs can generate ROS and stimulate the plants' defense pathway to fight oxidative stress damage (Shweta et al. 2016). Enzymes (such as SOD, CAT, POD (peroxidase), GPX and APX, thiol contents (GSSG or GSH), and malondialdehyde (MDA) content) are commonly changed as a result of the fluctuation of ROS concentration (Arif et al. 2016).

Multi-walled carbon nanotubes (MWCNTs) activate ROS defense response cascade, which prevents microbial pathogens from completing their life cycle. As compared to other metals and polymers, a very detailed study is done on the cerium oxide nanoparticles, which shows promising ROS scavenging enzymes mimicking activities. This property elevates the defense system in plants.

14.2.1 Chitosan Nanoparticles

Chitosan is a linear polymer composed of arbitrarily scattered D-glucosamine (deacetylated unit) and *N*-acetyl-D-glucosamine (acetylated unit) by the means of β-(1-4)-linkage. They are synthesized by treating the chitin shells of shrimp and other crustaceans with an alkaline solution (i.e., sodium hydroxide). Many naturally occurring polysaccharides are acidic in nature, but chitosan is the basic polymer occurring naturally.

Chitosan is widely used in cosmetics and substance-based applications. However, in current times biomedicine and agriculture have shown a rising interest in chitosan polymer as a therapeutic agent. It has been reported in the plant system that chitosan has the ability to induce multifaceted disease resistance (Hadrami et al. 2010). This naturally occurring biopolymer is widely studied for its significant properties like biocompatibility, biodegradability, nontoxicity, and antimicrobial activity, thus accepting its use as an initiator molecule for diverse host-pathogen interaction studies and analysis (Saharan et al. 2015; Prasad et al. 2017). These specific properties of chitosan can be further improved by using it in the structure of nanoparticles. In this structure it possesses quite different biological activities with distorted physicochemical features, i.e., size, surface area, cationic nature, etc. Its exclusive biocompatibility, biodegradability, and less poisoning nature make chitosan nanoparticles (CNP) a successful nano-transportation method than its close counterparts. However, the CNP are not only more stable and less poisonous, but also it does not require any complicated methods; it only needs use of uncomplicated preparative methods which make them a diverse and user-pleasant drug delivery mediator (Nagpal et al. 2010). Apart from biomedical implementations, CNP are only reported to have antifungal properties in response to different plant pathogens (Saharan et al. 2013). Nanoparticles by themselves can deal with cell walls and membranes more efficiently as compared to the foundation molecules from which they are prepared. Natural defense mechanism of plants relies upon early detection of pathogens. During evolution, plants have developed diverse mechanism to fight different evolving pathogens. The induction of natural defense mechanism involves overexpression of different defensive genes and enzymes, amplified deposition of phenolic compounds, cell wall synthesis, etc. Plants treated with different biological elicitor molecules have shown to provoke such innate immune response by mimicking variety of pathogens (McCann et al. 2012). As an exogenous elicitor, chitosan can stimulate resistance in plant host by increasing some defense-related enzyme activities, such as PAL, POD, CAT, SOD, and polyphenol oxidase (PPO) activities (Xing et al. 2015). Recently, Chandra et al. (2015) have reported that accumulation of CNP increases the plant defense by increasing the levels of SOD and CAT. CNP binds extracellular around the cell wall of the leaves. One of the most important signaling molecules is NO, which is also coupled with many physiological processes involving initiation of defense system in plants. Plants treated with CNP showed increased levels of NO, as compared to plants not treated with CNP (Raho et al. 2011; Malerba et al. 2012). CNP-treated sets resulted in upregulation of PAL activity leading to the higher level of phenolic compound accumulation. Phenylalanine ammonia lyase

(PAL), cinnamic acid 4-hydroxylase (C4H), and flavanone 3-hydroxylase (F3H) are the set of genes involved in flavonoid biosynthesis. PAL and C4H are important control points of phenylpropanoid biological synthesis. F3H is involved in flavonoid synthesis pathway in biological system yielding diverse family of flavonoid compounds possessing many types of activities, i.e., disease resistance. Higher accumulation of flavonoids like gallic acid (GA), epicatechin (EC), epigallocatechin (EGC), and caffeine was seen when sets were treated with CNP. These accumulated phytochemicals assist in adaptation to various environmental circumstances and provide resistance against pathogen by performing as feeding deterrents. In the presence of NADPH, anthocyanidin reductase (ANR) uses anthocyanidins as substrates to synthesize EC. EC ultimately changed to proanthocyanidins, which is commonly dispersed as plant defense compounds possessing intense toxicity toward pathogens. High levels of flavonoid deposition are an indication of improved resistance to plants. In CNP-treated plants higher expression of SOD and CAT was observed resulting in increased level of these enzymes. SOD and CAT are the essential antioxidant enzymes implicated in ROS scavenging system (Chandra et al. 2015). Polyphenol oxidase produce lignin from phenolic substances in angiosperm, it contributes in the thickening of cell wall structure and restricting pathogen entry (Li and Zhu 2013). ROS, Ca^{2+}, nitric oxide (NO), ethylene (ET), jasmonic acid (JA), salicylic acid (SA), and abscisic acid (ABA) all involved in chitosan-mediated signaling pathway (Xing et al. 2015). Nano-plant self-defense mechanism of the activated nano-chitosan through different modes of action such as pathogenesis involved proteins, defense-associated enzymes, and secondary metabolite deposition, in addition to the complicated signal transduction network (Fig. 14.1).

14.2.2 TiO_2 Nanoparticles

The activity of TiO_2 nanoparticles on the chloroplast aging of spinach in response to illumination was studied by Hong et al. (2005). Results represented that whenever chloroplasts were treated for 1, 5, and 10 min with 500 micromol/cm^2/min light intensity, the rate of oxygen liberation was speedily accelerated; when the chloroplasts were illuminated for 20, 30, and 40 min with 500 micromol/cm^2/min light intensity, the rate of oxygen liberation was statistically reduced. When spinach was treated with 0.25% TiO_2 nanoparticles, the rate of oxygen liberation of chloroplasts in various illumination times (1, 5, 10, 20, 30, and 40 min) was more as compared to control, and when illumination time was exceeded by 10 min, the reduction of the liberated oxygen rate was less as compared to control. Hong et al. (2005) concluded that TiO_2 nanoparticle treatment might defend chloroplasts aging for extended-time illumination. This mechanism represents that TiO_2 nanoparticle treatment significantly increases the defense properties of POD, SOD, and CAT. Decrease deposition of ROS and the level of malondialdehyde (MDA) maintain steadiness of membrane structure of chloroplast treated with luminance (Hong et al. 2005).CAT activity was increased (250–750 mg/kg) but was decreased in ascorbate peroxidase (APX) (500 mg/kg) when cucumber plants were treated with nano-TiO_2 (Servin

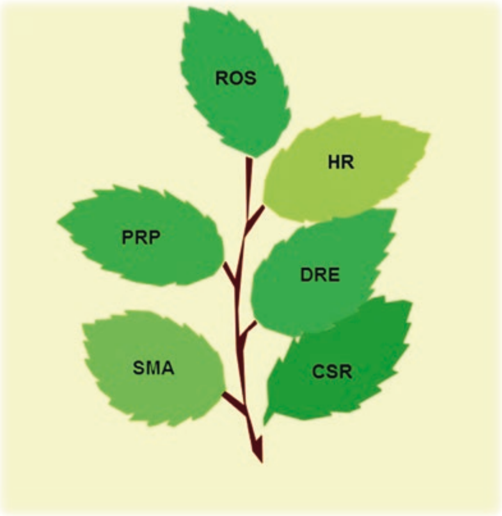

Fig. 14.1 Six plant defense responses to chitosan nanostructures including: reactive oxygen species (*ROS*), hypersensitive response (*HR*), pathogenesis-related proteins (*PRP*), defense-related enzymes (*DRE*), secondary metabolites accumulation (*SMA*), and complex signal transduction (*CSR*)

et al. 2013).The effect of nano-TiO_2 sprayed on pinto bean (*Phaseolus vulgaris*) was significant on activities of SOD, CAT, POD, MDA, and 8-deoxy-2-hydroxyguanosine (8-OHDG) content (Ebrahimi et al. 2016).

14.2.3 Multi-walled Carbon Nanotubes (MWCNTs) Nanoparticles

Multi-walled carbon nanotubes are diversely used in nanoscience in spite of concerns regarding probable poisonous effects. To conclude whether MWCNTs are toxic to *Oryza sativa* were treated with MWCNTs (Tan and Fugetsu 2009). Rice cells reacted with MWCNTs to develop aggregates that were analyzed using compound and scanning electron microscopy. Cell density gradually decreased with increased MWCNT concentration, probably representing a self-defense response. Thus, MWCNTs interact directly with rice cells and might have a damaging effect on rice growth and development. This property, although, was stronger as compared to carbon blacks; the rice cells survived the MWCNTs via self-defense mechanism (Tan and Fugetsu 2007). Tan et al. (2009) showed that when rice seedlings were exposed with MWCNTs, the ROS levels significantly increased and the cell viability decreased. This is because these nanotubes make contact with the cell walls and undergo ROS defense response cascade, which is ample to avoid microbial pathogens from finishing their life cycle (Smirnova et al. 2011). Moreover, Lin and Xing (2007) also observed apoptosis in cells of lettuce exposed to multiwall carbon nanotube.

14.2.4 Silicon Nanoparticles

Silicon is regarded as one of the most beneficial elements for the growth and development of plants which is available as second most abundant element of the Earth's crust (Epstein 1999; Tripathi et al. 2012a, b). It is accumulated by plant roots in the form of monosilicic acid and deposited in and between the plant cells which is called as phytoliths (Tripathi et al. 2012c, d, 2013, 2014, 2016b). In the form of phytolith deposition in plant cells, silicon provides the mechanical strength to plants from various biotic and abiotic stresses (Ma 2004; Tripathi et al. 2014, 2015b, 2016c, d, 2017d). Thus it will be more interesting and matter of great curiosity for the agricultural scientists to observe the behavior of silicon in the form of nanoparticles for the plants. In this connection in a study by Suriyaprabha et al. (2014), nanosilica treatment is screened for resistance in maize in response to plant pathogens such as *Fusarium oxysporum* and *Aspergillus niger* and comparative analysis done with bulk silica activity. The resistance is measured for pathogenicity index and expression of plant reactive compounds such as total phenolics, phenylalanine ammonia lyase, peroxidase, and polyphenol oxidase. The results represented higher expression level of phenolic compounds (2056 and 743 mg/ml) and a lower expression level of stress-responsive enzymes in response to both the fungi in nanosilica-treated plants. Maize expresses high resistance to *Aspergillus* spp., as compared to *Fusarium* spp. These results represent significantly elevated resistance in maize when treated with nanosilica as compared with bulk, especially at 10 and 15 kg/ha. However, hydrophobic potential and silica deposition quantity of nanosilica-treated maize (86.18° and 19.14%) are higher than bulk silica treatment. Hence, silica nanoparticles might be used as another potent antifungal agent against plant pathogens (Suriyaprabha et al. 2014). In addition Tripathi et al. (2017e) have reported the significant alleviative nature of silicon nanoparticles against the UV-B stress in wheat seedlings. Similarly, silicon nanoparticles have been also found to detoxify the arsenic and chromium stress in wheat and *Pisum sativum* seedlings, respectively (Tripathi et al. 2015a, b, 2016a, b, c, d, e).

14.2.5 Copper Oxide Nanoparticles

Copper oxide nanoparticles have brownish-black powder appearance. They are reduced to metal copper when treated with hydrogen or carbon monoxide in the presence of high temperature. They are harmful to humans and hazardous to ecosystem with detrimental consequence on aquatic life. CuO NPs are one of the most important and regularly used engineered oxide NPs with major industrial, medical, and environmental applications (Adhikari et al. 2012; Yadav et al. 2017). Nanoparticles are more vigorously deposited by plants. Nekrasova et al. (2011) reported that CAT and SOD activity are increased by the factor of 1.5–2.0 and lipid peroxidation activated when *Elodea densa* are exposed to copper oxide nanoparticles. In rice plantlets, nano-CuO treatment led to an amplified activity of antioxidant enzymes and increased MDA concentration (Shaw and Hossain 2013). Treatment with *n*CuO nanoparticles results in considerable oxidative stress i.e. higher ROS and MDA content with elevated actions of some anto-oxidative enzymes in rice (Da Costa and Sharma 2016; Shaw and Hossain 2013; Wang et al. 2015), wheat (Dimkpa et al. 2012), soybean (Nair and Chung 2014a), *Elodea densa* (Nekrasova et al. 2011), and *Arabidopsis thaliana* (Nair and Chung 2014b). It lead reduced CAT activity in alfalfa (Hong et al. 2015) and inhibited APX in Indian mustard (Nair and Chung 2015). A related assay on nano-CuO-mediated photosynthetic activity and antioxidative defense system in *Hordeum vulgare* revealed obstruction in root and shoot development with reduced photosynthetic performance index (Shaw et al. 2014).

14.2.6 Cerium Oxide Nanoparticles

Cerium has gained much attention of researchers from the field of physics, chemistry, metal science, and biology because it belongs to lanthanide group with 4f electrons. Formation of cerium oxide nanoparticles involves reaction between cerium and oxygen. This nanoparticle structure exhibits the fluorite crystalline structure that comes forward as charming material (Conesa 1995) variety of applications in engineering and biological arena involves effective incorporation of cerium oxide nanoparticles (Stambouli and Traversa 2002), high-temperature oxidation defense materials (Patil et al. 2002), catalytic materials (Trovarelli 1996; Kaspar et al. 1999), solar cells (Corma et al. 2004), and potential pharmacological agents (Celardo et al. 2011). CeONPs exhibit unique structure and atomic properties which result in its incorporation in the field of catalysis and stem cell research. In current years, CeONP has come under extreme study as a catalyst, as electronic, and as structural promoters of various catalytic reactions (Trovarelli 1996). In industries, it is applied as an active component more extensively in courses, i.e., three-way catalyst (Kaspar et al. 1999) for vehicle exhaust-gas treatments, oxidative union of methane, and water-gas shift reaction. Lately, CeONP reported to contain multienzyme including superoxide oxidase, catalase, and oxidase, mimicking properties. It has come into view as an attractive and profitable material in biological sciences such as in bioanalysis (Asati et al. 2009, 2011; Li et al. 2011; Ornatska et al. 2011; Kaittanis et al. 2012; Lin et al. 2012), biomedicine (Celardo et al. 2011), drug delivery (Xu et al. 2013; Li et al. 2013a), and bioscaffolding (Karakoti et al. 2010; Mandoli et al. 2010). Peroxide offers a source of hydroxyl radicals, which play a key role in oxidative damage. Das et al. (2007) concluded that the defensive effect of CeONP on the spinal cord implicates its free radical scavenging property (Fig. 14.2). In other reports, nano-CeO_2 increased H_2O_2 generation in corn (Zhao et al. 2012) and *Brassica rapa* (Ma et al. 2015b) but led to lower H_2O_2 in rice (Rico et al. 2013b, c). Exposure of sprouting rice seedlings to extremely concentrated CeONPs has disturbed free thiol levels, ascorbate, and enzyme activities leading to greater photosynthetic pressure and membrane injury in shoots (Rico et al. 2013a). Analysis of ROS scavenger activity indicated that behavior of SOD, CAT, APX, and POD was significantly elevated upon exposure to CeO_2 NPs, while these elevations were only evident for SOD and POD

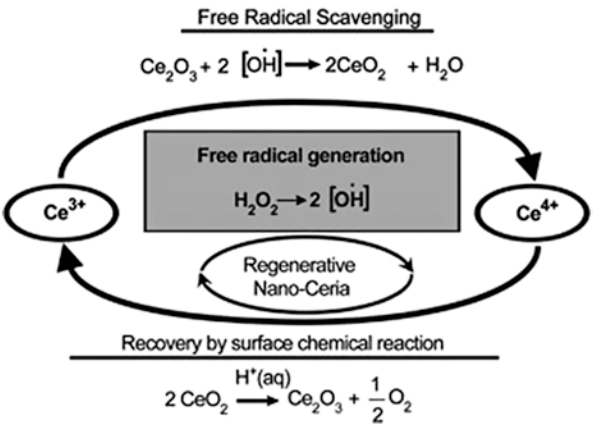

Fig. 14.2 Schematic detailing the proposed mechanism of the CeONP free radical scavenging property and autocatalytic behavior (Das et al. (2007) Copyright, Elsevier)

activities in the In_2O_3 NP treatments. Furthermore, the behavior of glutathione S-transferase (GST) and glutathione reductase (GR) was increased by approximately 15% and 51% by 1000 mg L^{-1} CeO_2 and In_2O_3 reaction. Moreover, activities of phenylalanine ammonia lyase (PAL) and polyphenol oxidase (PPO) were significantly induced in response to both types of NP (Ma et al. 2016).

The transportation mechanism of CeO_2 nanoparticles in plants and their effect on cellular homeostasis depending upon their exposure duration are not well understood. In a recent study, Majumdar et al.(2014) reported that kidney-shaped bean plants when treated with suspensions of ~ 8 ± 1 nm $nCeO_2$ (62.5–500 mg/L) for fortnight in hydroponic environment, the principal indicators of stress, i.e., lipid peroxidation, antioxidant enzyme activities, total soluble protein, and chlorophyll contents, showed certain. Cerium in tissues was localized and studied using scanning electron microscopy and synchrotron μ-XRF mapping. The chemical structures were identified using μ-XANES. In the root epidermis, cerium was shown to stay as $nCeO_2$; however, a small fraction (12%) was biotransformed to Ce(III) compound. Cerium reaches the root vascular tissues and translocates to upper parts of plant with time. Upon extended exposure to 500 mg $nCeO_2$/L, the root's antioxidant activity was extensively reduced, side by side elevating the solubilization of root protein by 204%. Guaiacol peroxidase is one of the most important ROS scavenging enzymes found in plants (antioxidants response to salinity and ameliorating its effect by *Nigella sativa*). The leaf's guaiacol peroxidase activity was improved with $nCeO_2$ introduction in order to sustain cellular homeostasis.

CeO_2 possesses various activities that make it most reliable metal nanoparticle to enhance the plant defense system. Few of the activities were documented: superoxide dismutase mimetic activity, catalase mimetic activity, nitric oxide radical scavenging, hydroxyl radical scavenging, peroxidase mimetic activity, oxidase mimetic activity, and phosphatase mimetic activity (Das et al. 2013; Nelson et al. 2016).

Recently Kuchma et al. (2010) concluded that molecules biologically related with phosphate ester (i.e., not DNA) can be hydrolyzed by CeONPs. Fascinatingly, they discovered dephosphorylation activity of CeONP depending on the presence of Ce^{3+} sites and restricted when Ce^{3+} is changed into Ce^{4+}. This opposes the thinning of Ce^{4+}-mediated hydrolysis by Qian and colleagues (Tan et al. 2008). To understand the pathway, further research is required.

14.2.7 Zinc Oxide Nanoparticles

Nano-Zn increased GSH levels and CAT activity in buckwheat leaves (Lee et al. 2013) (1-1000mg/ml) but showed no effect on APX activity (100–800 mg/kg) and reduced CAT activity (at 400 mg/kg) in corn leaves grown in soil amended with alginate (Zhao et al. 2013). Kim et al. (2012) noticed high activity for SOD, POD, and CAT when treated by nano-CuO and nano-ZnO in cucumber plants. ZnO NP exposure to the plants significantly promoted the growth rate, biomass, photosynthetic pigment levels, and protein content, while MDA production declined compared to the control. Interestingly, the ZnO NPs increased the action of antioxidant defense enzymes and upregulated the production level of SOD and POX isoenzymes in *Gossypium hirsutum* plants (Priyanka and Venkatachalam 2016). Production of ROS, RNS (reactive nitrogen species), and peroxide upon treatment with ZnO and Ag engineered NPs on the *Spirodela punctuta* shows the potential toxicity of Ag and ZnO nanoparticles principally grounded by the particulates and ionic forms (Thwala et al. 2013). SOD enzyme activity was increased after ZnO NP exposure, showing an amplification of the ROS scavenging process in *Spirodela polyrhiza* (Hu et al. 2013). The CAT and POX are notable antioxidant defense enzymes implicated in the detoxification of peroxide by changing free radicals to water and oxygen (Ma et al. 2015a, b).

14.2.8 Plant Induced Resistance

ROS not only restrict pathogen entrance but also play an important role in activating local and systemic defense systems such as the stimulation of pathogenesis-associated protein genes (Henry et al. 2013). The plant hormones salicylic acid, jasmonic acid, and ethylene participate significant roles in defense reactions as signaling molecules (Robert-Seilaniantz et al. 2011). The speedy production of O_2 or phenoxyl radicals in tomato roots treated with MgO NPs may play a related role in the resistance response of tomatoes against *Ralstonia solanacearum* (Imada et al. 2016). Chitosan extensively elevates polyphenol oxidase activity in rice plantlets followed by inoculation of two rice pathogens (*Xanthomonas oryzae* pv. *oryzae* and *X. oryzae* pv. *oryzicola*) (Li et al. 2013b). Silver and ZnO NP treatment lead to increase in contents of free radicals, together with ROS, reactive nitrogen species, and hydrogen peroxide in duckweed (Thwala et al. 2013). NPs discovered to induce oxidative stress and altered gene expression in plants (Wang et al. 2013).

14.3 Conclusion

The consequence of nanoparticles on gene expression with plant response to main supplies of environmental pressure leads the way to remediate the result of these possible harmful compounds through hormonal priming. Numerous studies are done dealing with plant response to the precise NP stress presenting differential mechanism involved in ROS detoxification, oxidation reduction, hormonal pathways and stress signaling. The mode of action of how NPs act on plant immunity maintenance has not been clarified. It is assumed that the mechanisms of NPs are possibly more complex than explained above, linking to a long way of actions, which need to further research and studies.

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Phytoengineered Nanomaterials and Their Applications

15

D. Mukundan and R. Vasanthakumari

Abstract

Phytoengineering deals with exploiting plants and green resources to provide solutions to various applications of science and engineering. Nanomaterials are particles which have one dimension at the minimum less than 100 nm and exhibit fascinating properties. There are a number of methods to synthesize nanomaterials which include physical, chemical, biological, and hybrid methods. Plant-mediated biological methods are being used by various researchers to synthesize nanoparticles of metal, metal oxides, and other materials with different size, shape, and quantity due to their easy availability and eco-friendliness. These nanoparticles are explored for various applications as potent antimicrobial agents, as electrochemical sensors and biosensors, in medicine and health care, in agriculture and crop biotechnology, and as pests, nutrients, and plant hormones and for their in vitro anticancer efficiency. This chapter reviews the research work done on phytoengineered nanomaterials, particularly metal, metal oxides, and other nanoparticles, using plant extracts, through in vitro synthesis using bacteria, fungi, yeast, algae, etc. and in vivo synthesis using phytomining and bioaccumulation of nanoparticles in live plants.

Keywords

Phytoengineering • Nanomaterials • Green synthesis • Plants • Microorganisms • In vitro • In vivo

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15.1 Introduction

In recent years, nanoscience and nanotechnology has been the subject of intense research, development, and commercialization. The applications of nanomaterials in industries are extremely wide and are found in various areas. The applications of nanoscience and technology in electronics and health care are immense and extremely familiar. Synthetic textiles fit in nanopowders providing the fabrics with antibacterial, flame-retardant, non-wetting, self-cleaning properties. Thick coatings which comprise nanometal oxides are utilized in water fast ink-jet media with photo-parity, while optical systems for light-emitting diodes employ thin coatings. Further applications are found in buildings and construction, automotive and aerospace components, environmental pollution reduction, and energy storage devices (Prasad et al. 2014, 2016).

Nanomaterials are particles comprising one or more dimensions less than or equal to 100 nm and have shown extensive attention due to their extraordinary attractive properties and applications which are more beneficial compared to bulk materials (Aziz et al. 2015). Numerous physical, chemical, biological, and hybrid methods are obtainable to synthesize diverse nanoparticles and used for various applications. Most of the nanomaterials used are mainly derived from physical, chemical, and other hybrid methods, but in recent years, several attempts have been made to prepare nanoparticles by green synthetic methods wherein the plant matter in any form is used to reduce the metal salts and other compounds. Various researchers have also reported eco-friendly methods to synthesize nanomaterials using microorganisms. Several microorganisms have been used to synthesize a number of inorganic nanoparticles with well-defined chemical composition, size, and shape and explored for various biological applications (Prasad et al. 2016). In addition to these, very recently green synthetic procedures are employed for preparation of nanomaterials by the plants themselves. Thus, it is of interest to consolidate and report an overview of the research work on nanomaterials from various parts of plant matter and also their in vitro and in vivo synthesis. This chapter provides a review on the research work done on phytoengineered nanomaterials, particularly metal and other nanoparticles using plant extracts, through in vitro and in vivo synthesis of plant matter.

15.2 Nanomaterial Synthesis

Nanomaterials deal with very fine structures with at least one dimension at the nanometre level which is one billionth of a meter. This has made the researchers think either ‘bottom-up’, where joining of atoms collectively occurs, or ‘top-down’, where breaking or dissociation of bulk matter into extremely small pieces containing only a few atoms occurs. This is entirely an interdisciplinary area including physics, chemistry, engineering, and medicine (Daniel and Astruc 2004).

There are many different ways of creating nanostructures and nanoparticles, viz. mechanical grinding, wet chemical synthesis, sol-gel process, gas phase synthesis, chemical vapour deposition (CVD), flame-assisted ultrasonic spray pyrolysis, gas condensation processing, sputtered plasma processing, microwave plasma processing, particle precipitation CVD, and pulsed laser ablation technique.

Among all these techniques, solution and wet chemical synthesis of nanomaterials have been a striking choice for research investigators, mainly because of the ease by which research can be accomplished in a laboratory.

Nanoparticle synthesis is mainly carried out by one of the chemical reaction methods either by metal alkoxide hydrolysis or metal salt precipitation with a base to get metal oxide nanoparticles or metal salt reduction with a reducing agent such as $NaBH_4$ or $LiAlH_4$ to synthesize metal nanoparticles or conversion of metal salts into sulfides, carbonates, etc.

15.2.1 Chemical Method of Preparation of Metal Nanoparticles

All chemical methods for the preparation of gold nanoparticles are based on the reduction of metal salts and their derivatives. However, in general, it is difficult to control the size of the nanoparticles, and in the absence of stabilizing agents, the particles tend to aggregate. For example, alkyl ammonium salts are used to stabilize Au nanoparticles, as they form a sort of 'electrical double layer' on the surface. This electrical double layer is weak, and hence the gold reactivity is not affected. For this reason, these nanoparticles are stable and cannot be separated from the solution from which they have been prepared. Here, the synthesis is usually performed in a two-phase (water/organic solvent) system. Alkyl ammonium salts like TOAB (tetraoctylammonium bromide), in addition to passivating the gold surface, do the task of phase transfer agents towards the Au(III) species to the organic phase.

Au nanoparticles, as well as other metal and metal oxide nanoparticles, can also be prepared inside a suitable block copolymer micelle in order to prevent the agglomeration of the nanoparticles. Reduction of the metal salt is performed with usual reagents (H_2, $NaBH_4$, hydrazine), and the steps involved in the preparation of any metal nanoparticle inside a micelle are given in Fig. 15.1.

There are a large number of papers regarding the synthesis, characterization, and applications of metal nanoparticles using wet chemical methods (Meng et al. 2010; Yuan et al. 2011; Bar et al. 2009; Jia et al. 2013; Wang et al. 2012; Liu et al. 2011; Luechinger et al. 2010; Tiwari et al. 2008).

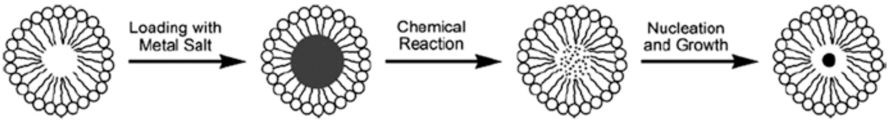


Fig. 15.1 Steps involved in the preparation of a metal nanoparticle inside a micelle

15.2.2 In Vitro Synthesis of Nanoparticles Using Extracts of Plant/Plant Parts

Green synthesis methods are more preferred over classical chemical methods due to the availability of more biological entities and eco-friendly procedures. The easy availability of various plant entities are highly explored for the biosynthesis of nanomaterials, particularly Ag-Au alloy composites and their morphologies (Monda et al. 2011) because nanomedicine is making a huge impact on healthcare sector in treating various chronic diseases. Hence, eco-friendly synthesis of nanoparticles from plant sources particularly from herbal plants is considered as important to control various diseases (Cruz et al. 2010; Kato 2011; Prasad 2014).

In vitro green synthesis methods have been developed using plant extracts for the bioreduction of metal ions to form nanoparticles. These methods offer added flexibility over the size and shape of the nanoparticles by changing the pH of the medium, controlling the reaction temperature conditions and also their effortless purification. The in vitro synthesis of nanoparticles occurs much faster because the reaction proceeds instantaneously, while the in vivo synthesis of nanoparticles requires the absorption and distribution of metal ions into the entire plant. The in vitro synthesis has been exhibited using various plant extracts combined with numerous acids and metal salts such as copper, gold, silver, platinum, iron, and other precursor salts (Khan et al. 2013; Rai and Yadav 2013; Prasad 2014).

Some examples include extracts of *Pelargonium graveolens* (rose geranium) reducing gold ions, stabilizing them to gold nanoparticles of decahedral icosahedral shape and 20–40 nm size, gold nanospheres, and nanotriangles of 0.05–18 μm synthesized using *Cymbopogon flexuosus* (lemon grass) extracts. Extracts of *Azadirachta indica* (neem plant) reduced tetrachloroauric acid to leveled gold triangles and hexagons having 50–100 nm size. The juice of *A. indica* reduced $AgNO_3$ to synthesize polydispersed spherical-shaped silver nanoparticles having a size of 5–25 nm (Shiv Shankar et al. 2004). Cubic-shaped In_2O_3 nanoparticles with 5–50 nm in size have been synthesized using the leaf extract of *Aloe barbadensis* (*Aloe vera*) (Maensiri et al. 2008).

Very recently, Kuppusamy et al. (2016) have reported a review on biosynthesized metallic nanoparticles from plant derivatives and their application in medical and commercial sectors including wastewater treatment, cosmetics, and food industry.

The different metallic nanoparticles such as gold, silver, platinum, zinc, copper, titanium oxide, magnetite, and nickel were synthesized from natural resources and have been studied exclusively. The different parts of plant such as stem, root, fruit, seed, callus, peel, leaves, and flower are used to synthesize metallic nanoparticles in various shapes and sizes by biological approaches. The research work carried out in green synthesis of various metal nanoparticles from various plant parts and their characterization and application areas are summarized in Tables 15.1, 15.2, 15.3, 15.4, 15.5, 15.6, and 15.7.

Table 15.1 summarizes the work done during synthesis of gold nanoparticles using the extracts of various plant parts and their properties and applications. The applications include antibacterial, antifungal, antioxidant, and anticancer activities.

Table 15.1 Synthesis of gold nanoparticles using extracts of plant/plant parts

Plant source/part	Characterization and salient features (size)	Applications	References
(a) *Salvia officinalis* leaves (b) *Lippia citriodora* leaves (c) *Pelargonium graveolens* leaves (d) *Punica granatum* fruit	SEM: 29–45 nm DLS: 30–70 nm Zeta potential: −12 to −24 TEM: 10–150 nm	In vitro – biocompatibility on L-cells	Paz Elia et al. (2015)
Black cardamom	TEM: 15–20 nm	N.A.	Ashwani and Srivatsava (2015)
Onion (*Allium cepa*)	XRD; SEM ~100 nm	In vitro – anticancer (MCF-7)	Umesh et al. (2011)
Citrus fruit (*Citrus limon*, *Citrus reticulata*, and *Citrus sinensis*) aqueous extract	TEM: 15–80 nm; XRD; DLS: 32–57 nm; zeta potential: 31−46	N.A.	Mohanan and Soundarapandian (2013)
Nepenthes khasiana leaf extract	SEM: 50–80 nm; TEM: 50 nm (spherical), 200 nm (triangular)	Antibacterial and antifungal	Bhau et al. (2015)
Couroupita guianensis flower	TEM: 7–48 nm	In vitro – anticancer (HL-60 cells)	Ravi et al. (2013)
Rosa hybrida petal extract	DLS: 10 nm TEM	N.A.	Masumeh et al. (2011)
Lavandula angustifolia – lavender leaf	DLS: 113.6 ± 56.9 nm TEM: 30–300 nm	Antioxidant activity – DPPH	Brajesh et al. (2016)
Diospyros ferrea	SEM	Antibacterial, antifungal, anticancer activity	Ramesh and Armash (2015)
Abelmoschus esculentus seed aqueous extract	XRD: 62 nm; AFM FESEM: 45–75 nm	Antifungal activity	Chidambaram et al. (2013)

Table 15.2 summarizes the work done during synthesis of silver nanoparticles using the extracts of various plant parts and their properties and applications. The studies include particularly the antimicrobial and antibacterial applications.

Table 15.3 shows the work done during lab synthesis of copper nanoparticles using the extracts of various plant parts and their properties and applications. The studies include particularly the catalytic applications for the synthesis of organic compounds in addition to antibacterial and anticancer activities.

Table 15.4 shows the research work done during lab synthesis of copper oxide nanoparticles using the extracts of various plant parts and their properties and applications. The studies include particularly the catalytic applications for the synthesis of organic compounds in addition to antibacterial activity.

Table 15.2 Synthesis of silver nanoparticles using extracts of plant/plant parts

Source	Characterization and salient features	Applications	References
Camomile plant	DLS: 7.5 nm TEM: 1.4 nm	Antimicrobial activity	Fariborz et al. (2014)
Lemon fruit	Particle size: 75 nm AFM image	*E. coli* *B. subtilis*	Praphulla et al. (2014)
Grape fruit (*Vitis vinifera*)	DLS: avg. 19 nm TEM: 18–20 nm	*E. coli* *B. subtilis*	Kaushik et al. (2013)
Dioscorea oppositifolia L. (Rhizome extract)	DLS: avg. 100 nm TEM: 14 nm	*E. coli* *B. subtilis* *K. pneumoniae* *P. aeruginosa* *B. cereus* *E. faecalis*	Uma Maheswari et al. (2012)
Leaves of: (a) *Ocimum tenuiflorum* (b) *Solanum trilobatum* (c) *Syzygium cumini* (d) *Centella asiatica* (e) *Citrus sinensis*	XRD: 20–60 nm AFM: 22–65 nm	*S. aureus* *P. aeruginosa* *E. coli* *K. pneumoniae*	Peter et al. (2015)
Coffea arabica – seed extract	DLS: 20–30 nm; XRD; TEM; SEM-EDAX	*E. coli* *S. aureus*	Vivek et al. (2016)
Azadirachta indica aqueous – leaf extract	TEM: approx. 34 nm; DLS: 34 nm	*E. coli* *S. aureus*	Shakeel et al. (2016)
Santalum album – leaf extract	SEM: 80–200; AFM	Antimicrobial activity	Swamy and Prasad (2012)
Syzygium cumini (jambul) – bark extract	SEM: 20–60 nm; AFM	Antimicrobial activity	Prasad and Swamy (2013)
Syzygium cumini (jambul) –leaf extract	SEM: 100–160	Antimicrobial activity	Ram Prasad et al. (2012)
Terminalia arjuna leaves	TEM: 8–16 nm; DLS: 3–50 nm [Average particle size: 5.20 nm]	*E. coli* *S. aureus*	Shakeel and Saiqa (2015)
Catharanthus roseus Linn. G. Don leaves	SEM-EDAX: 35–55 nm	Antiplasmodial – *P. falciparum*	Ponarulselvam et al. (2012)
Saraca indica – leaves	TEM: 23 ± 2 nm; DLS: 98 nm; SEM: 51–230 nm	*E. coli*, *P. putida*, *S. aureus*, *M. luteus*	Shyam et al. (2016)
Solanum lycopersicum – fruit extract	TEM: 13 nm	Insecticidal activity	Bhattacharyya et al. (2016)

Table 15.3 Synthesis of copper nanoparticles using extracts of plant/plant parts

Plant source/part	Characterization and salient features	Applications	References
Gymnema sylvestre leaves (aqueous and ethanol extracts)	SEM: 65–184 nm (aqueous), 181–302 nm (ethanol extract)	N.A.	Heera et al. (2015)
Datura innoxia leaves (aqueous extract)	UV-vis: 236–262 nm FESEM: 90–200 nm [Average Diameter: 5-15 nm]; EDAX	Antibacterial for *Xanthomonas oryzae* pv. *oryzae*	Antonysamy et al. (2016)
Citrus medica Linn. juice	Nanoparticle tracking analysis: 10–60 nm; XRD: 20 nm	Antibacterial, antifungal	Shende et al. (2015)
Ginkgo biloba L. leaf extract	TEM; EDS	Catalytic activity for Huisgen cycloaddition	Nazrollahzadeh and Sajadi (2015)
Euphorbia esula L aqueous leaf extract	XRD; TEM	Catalytic activity for ligand-free Ullmann coupling	Mahmoud et al. (2015)
Thymus vulgaris leaf and pedicle extract	XRD; FESEM-EDS; TEM: 56 nm	Catalytic activity for solvent-free synthesis	Akbar et al. (2015)
Phyllanthus emblica fruit extract	SEM	UV protection property on *Danio rerio*	Jyothi et al. (2016)
Carica papaya	UV-vis: 560 nm particle size: 20 nm	N.A.	Suresh et al. (2014a)
Potato starch	UV: 554 nm; SEM; XRD TEM: 5–40 nm; SERS	N.A.	Suresh et al. (2013)
Guava fruit aqueous	UV-vis: 294 nm SEM: 15–30 nm	Antibacterial activity *E. coli*, *S. aureus*	Caroling et al. (2015)

Table 15.5 shows the research work done during lab synthesis of iron oxide nanoparticles using the extracts of various plant parts and their properties and applications. The studies include particularly arsenic, lead, and cadmium removal and also coloured dye degradation applications in addition to water treatment for antibacterial activity.

Table 15.6 depicts the research work carried out during synthesis of zinc oxide nanoparticles using the extracts of various plant parts and properties and applications. The studies include particularly the photocatalytic degradation applications in addition to biomedical, antioxidant, and antibacterial activity.

The synthesis of noble metal nanoparticles such as platinum and palladium and metal oxide nanoparticles such as TiO_2, CeO_2, MgO, CdO, MnO_2, Cr_2O_3, HgO, ZrO_2, etc. from various plant parts are shown along with their multifaceted applications in Table 15.7.

Table 15.4 Synthesis of copper oxide nanoparticles using extracts of plant/plant parts

Plant source/part	Characterization and salient features	Applications	References
Gloriosa superba L. leaves	UV:380 nm; XRD: 8–17 nm; TEM: 5–10 nm	Antibacterial activity	Raja et al. (2015)
Punica granatum peels	UV: 282 nm; XRD: 40 nm	Mortality efficacy on green peach aphid	Ghidan et al. (2016)
Aloe vera leaf	UV: 270, 670 nm; TEM: 20–30 nm; XRD: 20 nm	Antibacterial against fish pathogens	Kumar et al. (2015)
Phyllanthus amarus leaves	UV: 285 nm; XRD: 22 nm; SEM: 50 nm	Antibacterial activity	Acharyulu et al. (2014)
Gum karaya	SEM; XRD; TEM; XPS	Antibacterial activity	Padil and Černík (2013)
Gundelia tournefortii aqueous extract	SEM; TEM; XRD	Catalytic activity for organic synthesis	Nasrollahzadeh et al. (2015)
Centella asiatica (L.) leaves	UV-vis; SEM	Catalytic activity on methyl orange	Henam and Thiyam (2014)
Pyrus pyrifolia leaves	XRD: 22 nm; UV-vis: 395 nm; ESEM: 24 nm; AFM: 22.5 nm	Photocatalytic activity on methylene blue	Sundaramurthy and Parthiban (2015)
Malva sylvestris leaves	XRD: 14 nm SEM: 5–30 nm	Antibacterial activity	Awwad et al. (2015)
Cassia alata flowers (aqueous)	UV: 263 nm SEM: 110–280 nm	N.A.	Jayalakshmi and Yogamoorthy (2014)

15.2.3 Typical Method of Preparation of Plant Extract and Synthesis of Nanoparticles

Most commonly employed methods of preparation of plant extract and subsequent synthesis of nanoparticles are given below. Whole plant or plant parts such as leaves, fruits, flowers, petals, roots, stem, peels, and seeds were washed thoroughly with water and shade dried for 5–7 days. Required plant part extract in water was prepared using cold/Soxhlet extraction or by heating to 60–80 °C using known quantity of the plant part and water. The extract was kept frozen or at 4 °C until further use. In some cases, the preparation of leaf and fruit extracts was done by washing with tap water and double-distilled water followed by homogenization, centrifugation, filtration, and storing the aqueous extract at −18 °C until use.

For the synthesis of nanoparticles, known quantity of precursor salt (e.g. silver nitrate, auric chloride, copper acetate monohydrate, etc.) was dissolved in a known volume of deionized water and treated with a known volume of plant aqueous extract and kept at room temperature/boiled for few minutes. Subsequent change in the colour of the solution clearly indicates the formation of nanoparticles. This solution was further centrifuged at 5000–15,000 rpm for nearly 10–30 min. The

Table 15.5 Synthesis of iron oxide nanoparticles using extracts of plant/plant parts

Plant source/part	Characterization and salient features	Applications	References
Hordeum vulgare aqueous *Rumex acetosa* aqueous	TEM:10–40 nm EELS; XPS; DLS	Antioxidant	Valentin et al. (2014)
Eucalyptus globulus/ chitosan matrix	XRD: maghemite structure	Efficient arsenic removal	María et al. (2016)
Mangifera indica leaves (mango)	FESEM: nanorods HRTEM: length – 15 ± 2 nm	Heavy oil viscosity treatment	Majid S Al Ruqeishi et al. (2016)
Citrus medica fruit (Al-Abbas's (A.S.) Hund) extract	UV: 340 nm XRD: 45 nm SEM: spherical	River water treatment to kill bacteria	Esam J. AL-Kalifawi (2015)
Nephelium lappaceum (rambutan) peel waste	XRD; Raman spectroscopy; TEM: 200 nm	Green ligation and chelating agent	Yuvakkumar and Hong (2014)
Green tea leaves	TEM: 40–60 nm EDX; XPS	Fenton-like catalyst for cationic and anionic dyes	Shahwan et al. (2011)
Padina pavonica (Linnaeus) Thivy and *Sargassum acinarium* (Linnaeus) Setchell	UV:402–415 nm Particle size:10–19.5 nm and 21.6–27.4 nm	Bioremediation Lead removal	Hala Y El-Kassas et al. (2016)
Tangerine peel extract	DLS: 200 nm; SEM	Cadmium removal	Mohammad et al. (2015)
Murraya koenigii leaf extract	UV:277 nm; FTIR TEM: spherical (~59 nm)	Fermentative hydrogen production	Mohanraj et al. (2014)
Piper betle leaves	SEM; AFM TEM: spherical (16 nm)	Dye degradation – decolourization of malachite green and methyl orange	Badmapriya and Asharani (2016)

nanoparticles thus obtained were collected and resuspended in double-distilled water three times to remove the impurities and used for characterization using FTIR, UV-vis spectroscopy, SEM, TEM, XRD, etc.

15.2.4 Parameters Influencing the Synthesis of Nanoparticles in Plant Extracts

The synthesis of nanoparticles through reduction of metal ions is affected by a large number of parameters in addition to the nature of the plant comprising the active phytochemicals in different combinations and concentrations and other parameters such as pH (Gan and Li 2012; Ghodake et al. 2010; Armendariz et al. 2004; Sathishkumar et al. 2010; Lukman et al. 2011; Cruz et al. 2010; Das et al. 2011), time required for the reaction, concentration of the precursor and plant extract, required temperature, applied pressure, and electrochemical potential of a metal ion

Table 15.6 Synthesis of zinc oxide nanoparticles using extracts of plant/plant parts

Plant source/part	Characterization and salient features	Applications	References
Aloe barbadensis miller leaf extract	TEM: 25–40 nm	Biomedical and cosmetics	Sangeetha et al. (2011)
Cassia fistula plant extract	UV: 370 nm TEM: 5–15 nm (hexagonal wurtzite)	Photodegradative Antioxidant Antibacterial	Suresh et al. (2015)
Coffee powder extract	TEM; SEM; EDAX	Stability and activity of proteinase K	Mansoore et al. (2016)
Aloe vera leaf extract	XRD: 22.18 nm hexagonal	Photocatalytic degradation – fluorescein dye; antibacterial	Varghese and George (2015)
Punica granatum peel extract	UV: 364 nm SEM: 50–100 nm spherical and square	Antifungal	Vijaylaxmee and Sharma (2015)
Catharanthus roseus Linn. G. Don leaf extract	XRD: hexagonal wurtzite SEM: 23–57 nm spherical	Antibacterial	Bhumi and Savithramma (2014)
Moringa oleifera leaf extract	XRD: hexagonal wurtzite	Antibacterial and antifungal	Elumalai et al. (2015)
Azadirachta indica gum	XRD: 13–15 nm (hexagonal wurtzite) FESEM: 30–60 flower shaped	Antibacterial	Geetha et al. (2016)
Terminalia chebula fruit extract	XRD: hexagonal wurtzite	Photocatalytic – rhodamine B	Rana et al. (2016)
Azadirachta indica leaf extract	TEM: 9.6–25.5	Antibacterial and photocatalytic	Bhuyan et al. (2015)
Citrus aurantifolia (lemon fruits)	FESEM: 21.5 nm	Photocatalytic activity	Fatemeh et al. (2015)

(Raveendran et al. 2003; Haverkamp and Marshall 2009; Selvakannan et al. 2004). All these factors lead to change in size, shape, and morphology of nanoparticles.

Figure 15.2 shows different sizes and shapes of the nanoparticles derived from plant resources. Biosynthesis reaction can be altered by a wide range of metal concentration and amount of plant extract in the reaction medium; it may transform the shapes and sizes of the nanoparticles (Chandran et al. 2006; Dubey et al. 2010).

Mukundan et al. (2017) have synthesized silver, gold, and silver-gold composite nanoparticles using the leaf extract of *Bauhinia tomentosa* Linn. and characterized their properties using UV-vis spectroscopy, FTIR, XRD, SEM, EDAX, and HRTEM (Fig. 15.3). The authors have chosen this plant due to it its versatility, most commonly used as a household remedy for curing many diseases.

Table 15.7 Synthesis of other nanoparticles using extracts of plant/plant parts

Plant source/part	Characterization and salient features	Applications	References
Psidium guajava, *Calotropis gigantea* flower, *Vigna radiata* – green gram seed extract (TiO_2)	FESEM: spherical/oval shape XRD: 10.5–32.6 nm	Antibacterial, antioxidant, antiparasitic, and anticancer	Santhoshkumar et al. (2014), Sampath et al. (2013) and Ankita et al. (2016)
Gloriosa superba leaf; *Aloe vera* extract (CeO_2)	XRD: cubic structure TEM: 5 nm spherical	Antibacterial and antioxidant activity	Ayyakannu et al. (2015) and Debanjan et al. (2016)
Azadirachta indica, neem; *Quercus glauca* leaves; *Diospyros kaki* leaf extract (Pt)	TEM: 5–50 nm spherical UV: 210–477 nm TEM: 2–20 nm sphere and plates	Electrochemical oxidation	Thirumurugan et al. (2016), Karthik et al. (2016) and Song et al. (2010)
Hippophae rhamnoides Linn. leaf; *Evolvulus alsinoides* leaf extract (Pd)	XRD: 5 nm; TEM: 5 nm; DLS: 5 nm	Catalytic activity; in vitro anticancer efficacy on human ovarian A2780 cells	Mahmoud et al. (2015) and Sangiliyandi et al. (2015)
Nephelium lappaceum, *Brassica oleracea*, and *Punica granatum* peels (MgO)	SEM: spherical; XRD: 24–70 nm; ZETA: 29.2 ± 1.5–30.5 ± 1 mV	Natural ligation agent; anticancer (HeLa cells) and photocatalytic	Suresh et al. (2014b) and Sugirtha et al. (2015)
Fenugreek seed powder and *Vitis vinifera* (raisin) extract (Se)	SEM: 50–150 nm oval XRD: 12 nm TEM: 28 nm spherical	Anticancer MCF7 cells; pharmaceutical	Ramamurthy et al. (2013) and Garima et al. (2014)
Papaya peel extract (CdS)	XRD: 2.7 nm; HRTEM: 2.3–3.2 nm	Biosensors	Bhuvaneswari and Radjarejesri (2015)
Achillea wilhelmsii flower (CdO)	UV: 300 nm FESEM: 35 nm	N.A.	Javad and Sasan (2013)
Raphanus sativus var. *longipinnatus* leaf and *Piper longum* fruit extract (Co)	UV: 448 nm SEM: 80 nm spherical	In vitro anticancer – antibacterial, electrocatalytic activity	Rama et al. (2016) and Ranaei Siadat (2015)
Lemon extract (Mn)	UV: 360 nm TEM: 50 nm spherical	Antifungal, antibacterial	Jayandran et al. (2015)
Sapindus mukorossi (MnO_2)	FESEM: below 100 nm TEM: 28.1–63.1 nm needle, spherical, and cubic shapes	Catalysts for the oxidation and polymerization of aromatic amines like p-anisidine, p-chloroaniline, aniline	Vidhisha et al. (2016)

(continued)

Table 15.7 (continued)

Plant source/part	Characterization and salient features	Applications	References
Arachis hypogaea leaves; *Mukia maderaspatana* plant extract (Cr_2O_3)	UV: 458 nm; XRD: 60–80 nm; SEM hexagonal and cubic	Antibacterial; electrochemical catalytic activity	Ramesh et al. (2012) and Rakesh et al. (2013)
Citrus aurantifolia (lemon fruits); *Acalypha indica* leaf extract (ZrO2)	XRD: 20 nm cubic and monoclinic phase SEM: 20–100 nm cube	Electrolyte material in the intermediate temperature solid oxide fuel cells	Ali et al. (2016) and Shanthi Sri Nisha (2016)
Callistemon viminalis flower extract (HgO)	UV: 243 nm; XRD: cubic crystal; TEM: 2–4 nm spherical	Antimicrobial activity	Das et al. (2015)

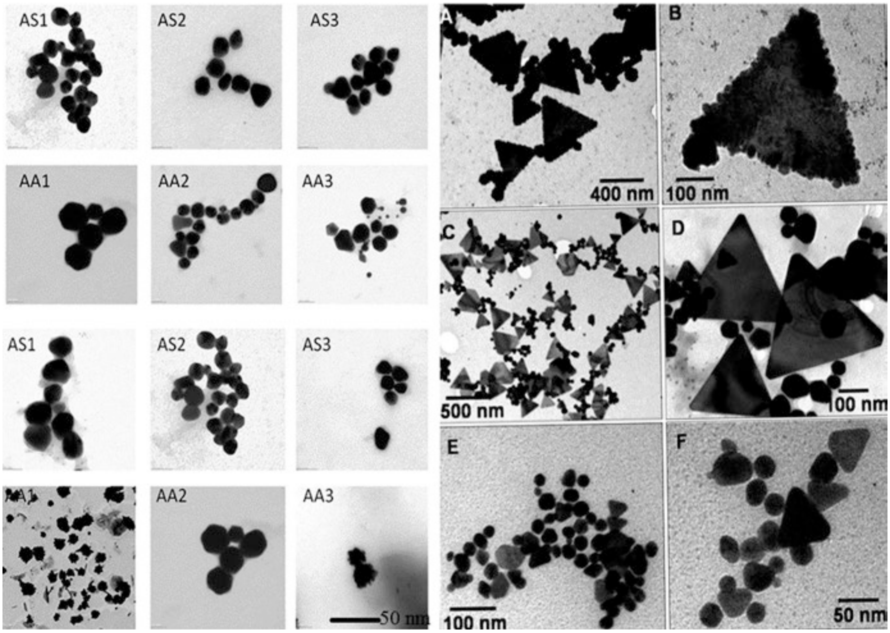


Fig. 15.2 TEM images of gold nanotriangles and various shapes synthesized using different amounts of *Aloe Vera* extract [(**a**, **b**) 0.5 mL; (**c**, **d**) 1 mL; (**e**, **f**) 4 mL] by reaction with 6 mL of 10–3 M $HAuCl_4$ (Dubey et al. 2010)

It is also interesting to find that Ag-Au core-shell nanoparticles are formed in the Ag-Au composites at different compositions prepared using the *B. tomentosa* extract. The UV-vis spectroscopy of Ag-Au composite prepared by green synthesis using *B. tomentosa* shows clearly this information (Fig. 15.4). Mostly it has been

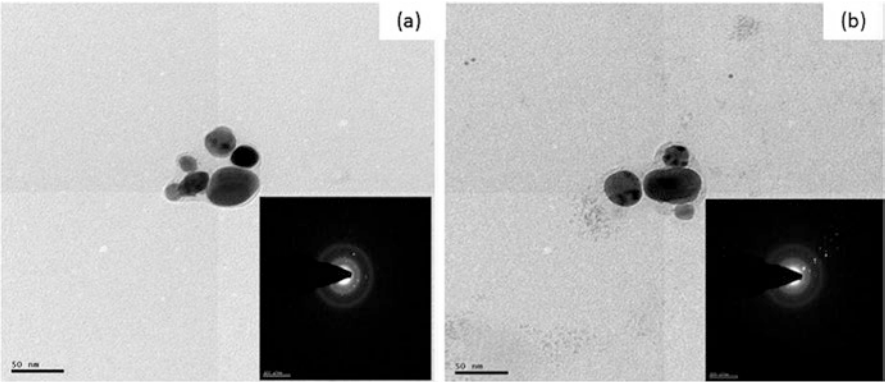


Fig. 15.3 HRTEM of (**a**) Ag nanoparticles and (**b**) Au nanoparticles (Mukundan et al.)

found Au core and Ag shell nanoparticles were formed, and only when Ag seed followed by Au is added, it leads to Ag core and Au occupying the shell [Samal AK et al. (2013)].

Figure 15.5 shows the HRTEM images obtained from Ag-Au composites which depict core-shell structure of the composite. Hence, both UV-vis spectra and TEM pictures suggest that the green synthesis using *B. tomentosa* gives Ag-Au core-shell structures. The reasons for the formation of Ag core with Au shell are not clear. This needs to be studied further.

15.2.5 Hydrothermal Process of Synthesis of Nanoparticles from Plant Extracts

Numerous researches have been done to synthesize metal, metal oxide, and other nanoparticles using hydrothermal process employing high temperature and high pressure reactions in an autoclave to get nanoparticles of increased size and shape. This hydrothermal process involving both temperature and pressure can lead to more productivity of the nanomaterials. Very recently efforts are being taken by researchers to carry out biomaterial-mediated hydrothermal synthesis. Chitosan, cellulose, etc. are tried to prepare mesoporous silver nanopowder, magnetite nanoparticles (Quang and Chau 2013; Santi et al. 2013; Li et al. 2014; Ying-fen et al. 2015). The plant extract-mediated hydrothermal process can prove to be a good method of getting large quantity of metal, metal oxide, and other nanoparticles in the future which can be exploited for commercial applications.

Ramar et al. (2015) have carried out hydrothermal synthesis of AgNPs using *B. tomentosa* Linn. leaf extract and silver nitrate for different reaction periods, namely, 1, 3, and 5 h at temperatures 150–180 °C. They have found an increase in particle size with time and temperature as shown by UV-visible absorption spectra (Fig. 15.5) and XRD (Fig. 15.6). With the increase in hydrothermal process time, the intensity of absorption band changes.

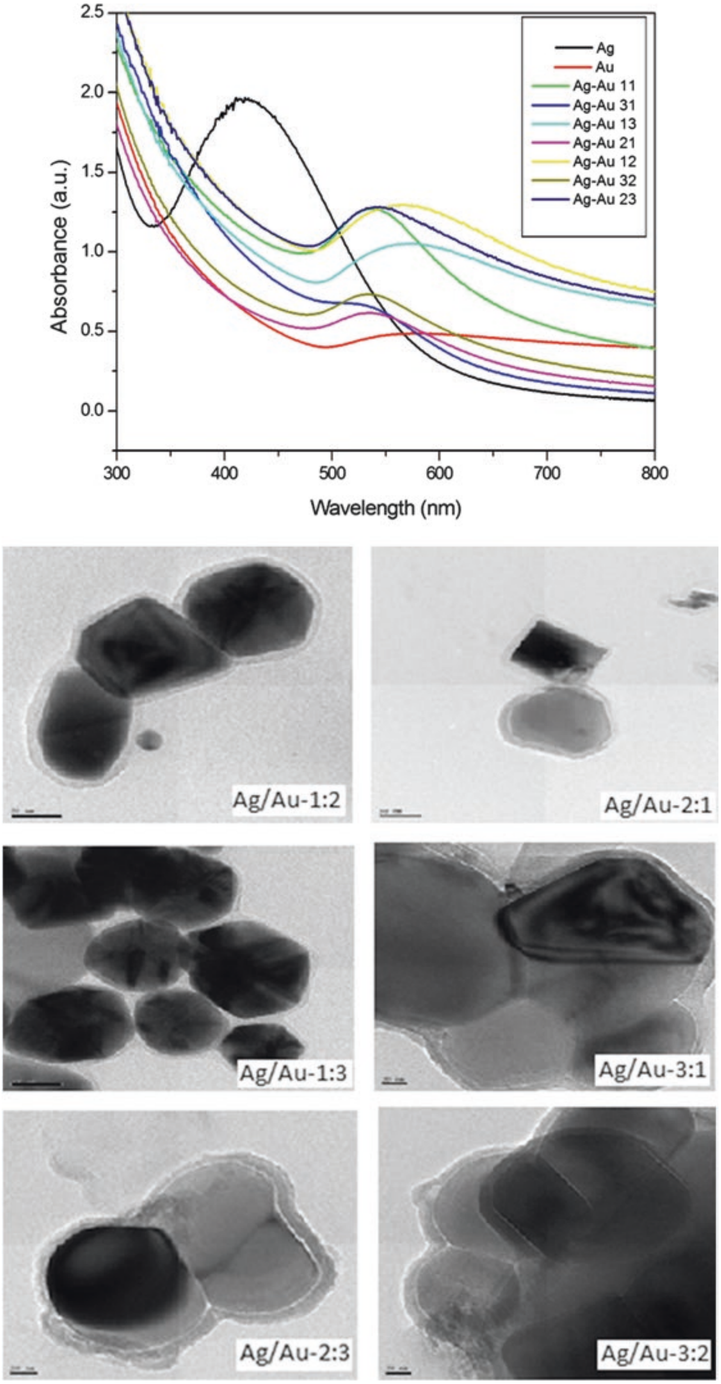


Fig. 15.4 (**a**) Depicts the UV-Visible spectra; (**b**) Depicts HR-TEM images

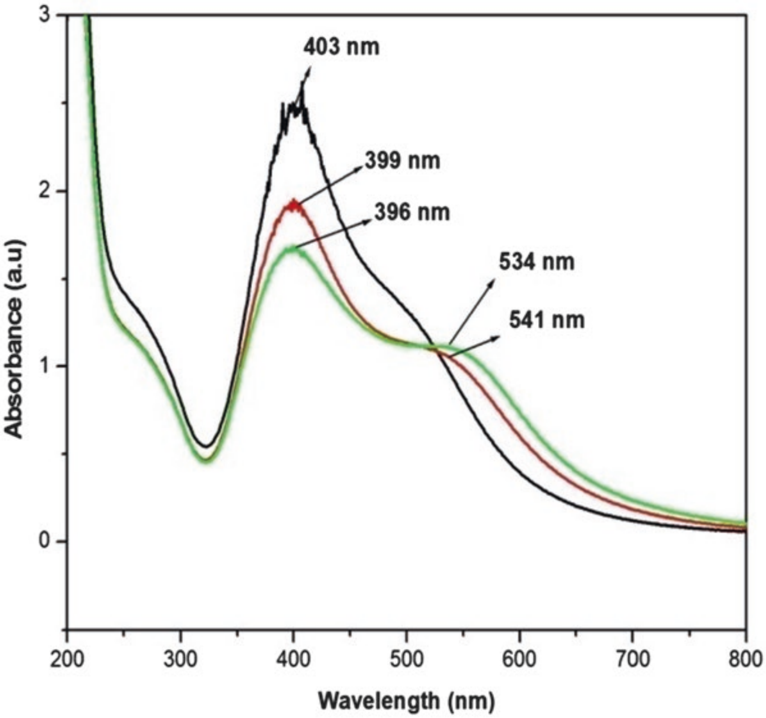


Fig. 15.5 UV-visible spectrum of AgNP prepared at 150 °C at 1, 3, and 5 h (Ramar et al. 2015)

15.2.6 Mechanism of Nanoparticle Formation in Plant Extracts

It has been shown with FTIR that plant crude extract contains several phytochemicals such as carbohydrates, terpenoids, polyphenols, alkaloids, phenolic acids, and proteins that play a vital role by reducing metal ions to metal nanoparticles, thereby stabilizing them (Song et al. 2010; Song and Kim 2009; Shanthi and Sri Nisha Tharani 2016). It is mentioned that control over the size and morphology of nanostructures may be connected to the interaction of these phytochemical molecules with metal ions (Bhau et al. 2015). All the plants do differ in the concentration and composition of these phytochemicals, and this partly explains the morphological differences of the nanoparticles such as triangles, hexagons, pentagons, cubes, spheres, ellipsoids, nanowires, and nanorods. The change in the morphology and size of nanoparticles synthesized from a variety of metal ions in extracts of various plants has been described in detail in the review by Haverkamp and Marshall (2009).

Given below is the typical biochemical reaction of precursor salts with the plant extract to the formation of nanoparticles such as Ag, Au, Cu, Pt, and ZnO:

Metal salts + plant phytochemicals → Metal NPs + by – products

Various plant metabolites, including terpenoids, polyphenols, sugars, alkaloids, phenolic acids, and proteins, which are responsible for the bioreduction of metal ions, yielding nanoparticles are shown in Fig. 15.7.

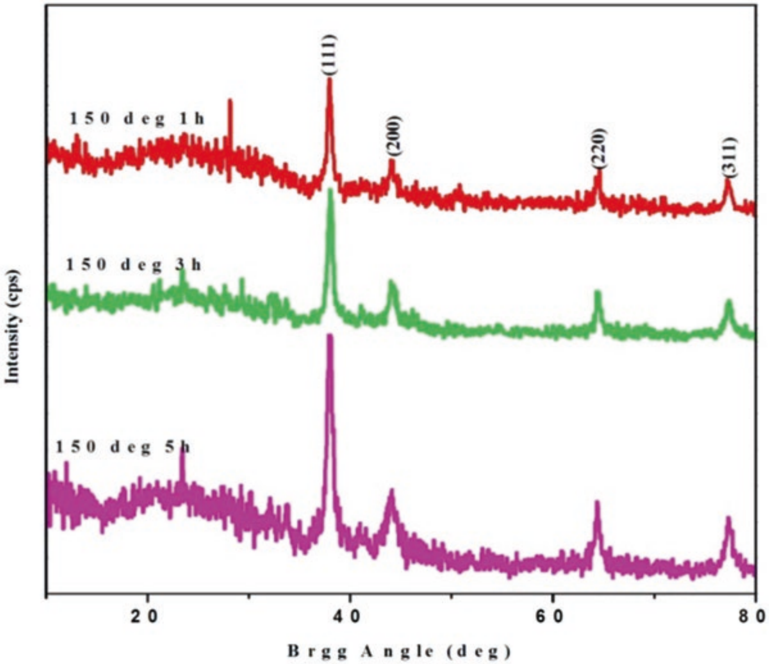


Fig. 15.6 XRD pattern of synthesized AgNP (Ramar et al. 2015)

FTIR spectroscopy shows that terpenoids in plants or plant extracts are more often involved in the synthesis of nanoparticles. Terpenoids, synthesized in plants using five-carbon isoprene units, are a class of different organic polymers which exhibit strong antioxidant activity. It has been suggested that the phytoconstituents play an important role by reducing metal salts to respective metal ions and finally form nanoparticles (Shiv Shankar et al. 2004). Flavonoids belonging to a group of polyphenols can reduce metal ions into nanoparticles along with anthocyanins, isoflavonoids, flavonols, chalcones, flavones, and flavanones. The various functional groups present in flavonoids help in the formation of nanoparticles. The keto-enol tautomeric transformation of flavonoids might release a reactive hydrogen atom which has the ability to reduce metal ions to nanoparticles.

The mechanism of synthesis of metal nanoparticle in plants and plant extracts occurs in three segments, namely, initiation, propagation, and termination. During initiation, reduction of metal ions and nucleation of the reduced metal atoms occur. Propagation involves the spontaneous coalition of small nanoparticles into particles of larger size to increase the thermodynamic stability of nanoparticles, while termination offers the final energetically favourable conformation/shape to form nanotubes/prisms/hexahedrons and a number of asymmetrical nanoparticles with the organic coating around the particle

The schematic representation of the synthesis of nanometal particle is shown in Fig. 15.8.

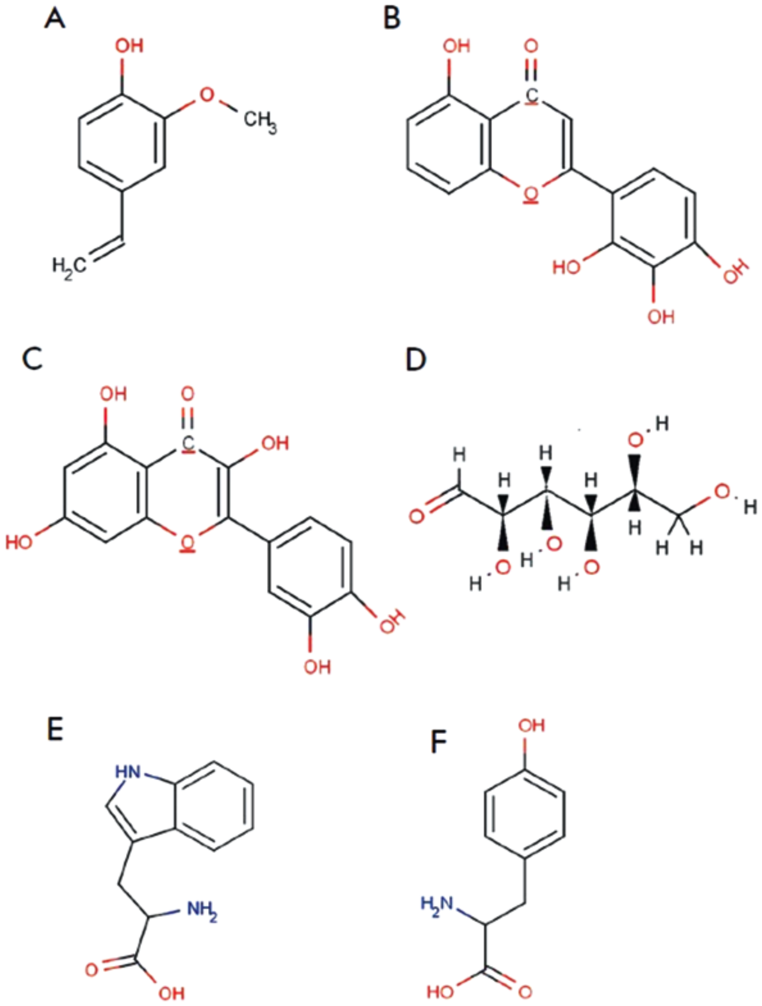
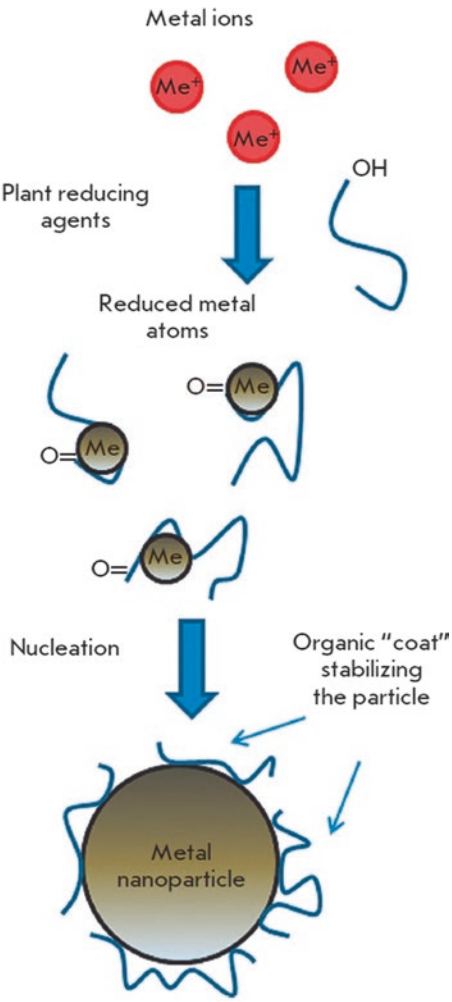


Fig. 15.7 Main plant metabolites: (**a**). terpenoids (eugenol); (**b**, **c**) flavonoids (luteolin, quercetin); (**d**) a reducing hexose with the open-chain form; (**e**, **f**) amino acids

15.2.7 In Vitro Synthesis of Nanomaterials Using Microorganisms

As seen earlier, the biosynthesized nanoparticles have been used in a variety of applications including drug carriers for targeted delivery, cancer treatment, antimicrobial agents, biosensors, catalysts for enhancing rate of the reaction, filtration processes, and magnetic resonance imaging (Mohanpuria et al. 2008; Grass et al. 2010). A lot of efforts are being taken to synthesize nanomaterials from extracts of various plant parts as shown in the earlier section. It will be more advantageous if the reduction processes could be carried out by specific microorganisms by which

Fig. 15.8 Schematic representation of synthesis of metal nanoparticle using plant extracts as reducing agents



the productivity of the nanoparticles of specific size and shape can be achieved. This has led many researchers to give more importance towards the reliable, green methods using specific chosen microorganisms in synthesis of nanoparticles and to work on the in vitro synthesis of nanomaterials using microorganisms both at the intracellular and extracellular level.

A diverse range of inorganic nanoparticles with well-defined size, shape, and morphology have been synthesized using different microorganisms, and their technological application areas have been explored. This biological process is more acceptable, is not energy intensive, and is also eco-friendly. This biogenic approach involved with microorganisms and metal salts at ambient conditions such as temperature, pH, pressure etc., and the nanoparticles synthesized by this process are of higher catalytic reactivity, greater specific surface area, and so on.

Microorganisms have the ability to synthesize inorganic materials such as silica, magnetite, gypsum, and calcium carbonate layers and minerals such as calcite into functional super nanostructures. Thus, it creates interest to exploit microorganisms such as bacteria and fungi for nanomaterial synthesis. Cadmium sulfide nanoparticles' synthesis with different sizes and shapes makes great importance for their applications in the field of optical devices, electronics, biomedical, and biotechnology (Li et al. 2011).

Thus, nanomaterials are biosynthesized when the microorganisms are made to have contact with required metal ions into the element metal through enzymes generated by the cell activities. This reaction can be intracellular and extracellular based on the location of formation of nanoparticles. The intracellular method involves conversion of metal ions to metal nanoparticles inside the cell of microbes in the presence of enzymes, while the extracellular synthesis involves trapping of metal ions on the microbial cell surface and their reduction enzymatically (Zhang et al. 2011; Abd El-Raheem R El-Shanshoury et al. (2011).

Xiangqian Li et al. (2011) have provided a brief overview about the recent research on the biological synthesis of metallic, oxide, sulfide, and other types of nanoparticles in their review article. The mechanism of bioreaction, the conditions required for controlling the size and shape of the particles, the biosynthesis of monodisperse nanoparticles, and their current applications in nanomedicine and biological fields have been discussed. The final conclusions were regarding the limitations and prospects of nanoparticle synthesis by microorganisms.

15.3 Metal Nanoparticles

Extracellular synthesis of gold nanoparticles by fungus *Fusarium oxysporum* and actinomycete *Thermomonospora* sp. (Ahmad et al. 2003a, b) and intracellular synthesis of gold nanoparticles by fungus *Verticillium* sp. (Mukherjee et al. 2001) have been reported by Sastry and coworkers. The precipitation of gold nanoparticles inside the bacterial cells by incubation with Au^{3+} ions has been established by Southam and Beveridge (1996). Gold nanoparticles with uniform dispersity have been synthesized using alkalotolerant *Rhodococcus* sp. under extreme alkaline and considerably high temperature. (Ahmad et al. 2003a, b). Synthesis of gold nanostructures (spheres, cubes, and octahedron) by filamentous cyanobacteria from Au(I)-thiosulfate and Au(III)-chloride complexes and their mechanism of formation have been reported. Growth of nanocrystals and nanoalloys using *Lactobacillus* has been reported by Nair and Pradeep. The synthesis of nanoparticles by microorganisms gives monodisperse nanoparticles, while synthesis by chemical methods or plant extracts shows enormous variations in the particle size.

Table 15.8 gives the various metal nanoparticles synthesized by different microorganisms and their shapes along with their location.

Researchers have also identified and used various microbes for the synthesis of silver nanoparticles which are found to reduce the Ag^+ ions to AgNPs and most of which form spherical particles (Mukherjee et al. 2001; Ahmad et al. 2003a, b;

Table 15.8 Metal nanoparticle preparation by different microorganisms

Metal NPs	Microorganisms	Shape	Location	References
Au	*Sargassum wightii*, *Rhodococcus* sp. *Shewanella oneidensis* *Plectonema boryanum* *Plectonema boryanum UTEX 485* *Candida utilis* *V. luteoalbum* *Escherichia coli* *Yarrowia lipolytica* *Pseudomonas aeruginosa* *Rhodopseudomonas capsulata* *Shewanella algae* *Brevibacterium casei* *Ureibacillus thermosphaericus* *Fusarium oxysporum* *Neurospora crassa* *Yeast*	Planar, spherical, cubic, octahedral, triangles, hexagons, pyramidal, polygonal	Intracellular Extracellular	Nisha et al. (2014), Zhang and Fang (2010), Song and Kim (2009), Liu et al. (2006), Kumar et al. (2012), Biswas and Wu (2005), Navarro et al. (2008), Mondal et al. (2011), Monica and Cremonini (2009), US EPA (1996), Lin and Xing (2007), and Stampoulis et al. (2009)
Ag	*Trichoderma viride* *Phanerocheate chrysosporium* *Bacillus licheniformis* *Brevibacterium casei* *Escherichia coli* *Corynebacterium glutamicum* *Bacillus cereus* *Aspergillus flavus* *Aspergillus fumigatus* *Verticillium* sp. *Neurospora crassa* *Yeast Fusarium oxysporum*	Spherical, pyramidal, polygonal	Intracellular Extracellular	Brooks and Robinson (1998), Husen and Mishra (2002, 2003, 2008), Burris et al. (2012), Doshi et al. (2008), Roghayyeh et al. (2010), Miao et al. (2007), Musante and White (2010), and Barrena et al. (2009)
Pt	*Shewanella algae*		Intracellular	Feng et al. (2013)
Hg	*Enterobacter* sp.	Spherical	Intracellular	Dimkpa et al. (2013)
Se	*Shewanella* sp.	Spherical	Extracellular	Abou El-nour et al. (2010)
CdTe	*Escherichia coli*	Spherical	Extracellular	Priyadarshini et al. (2013)
U, Tc, Cr, Co, Mn	*Pyrobaculum islandicum*	Spherical	Extracellular	Kumari et al. (2009)
Pd	*Desulfovibrio desulfuricans*	Spherical	Extracellular	Kim et al. (2007)

Fayaz et al. 2010). An aqueous solution of silver nitrate was reduced by *Pseudomonas stutzeri* AG259, a bacterium isolated from silver mines, to synthesize AgNPs of well-defined size and distinct shape within the bacterial periplasmic space (Klaus et al. 1999). Synthesis of AgNPs in the form of a film on the surface of the fungal cells *Verticillium*, *Fusarium oxysporum*, and *Aspergillus flavus* has also been reported (Jain et al. 2011; Vigneshwaran et al. 2007; Bhainsa and D'Souza 2006; Senapati et al. 2004).

Zheng et al. (2010) have studied and reported Au-Ag alloy nanoparticles biosynthesized via the extracellular way by yeast cells. TEM characterization showed the formation of irregular polygonal Au-Ag alloy nanoparticles. Synthesis of core-shell Au-Ag alloy nanoparticles by fungal strains *Fusarium semitectum* and the high stability of nanoparticles for several weeks has been studied and reported by Sawle et al. (2008).

15.3.1 Heavy Metal Nanoparticles

Heavy metals are toxic to the life of microorganisms. The resistance of microbes to a majority of toxic heavy metals is mainly because of their chemical detoxification system and energy-dependent ion efflux from the cell by proteins from the membrane which function as ATPase or chemiosmotic cation or proton anti-transporters. Microbial resistance also depends on the alteration in solubility. Synthesis of platinum nanoparticles of 5 nm size on the periplasm using resting cells of the bacterium *Shewanella algae* which reduced aqueous Pt ions into elemental Pt at room temperature and pH 7.0 within an hour with lactate as the electron donor has been reported (Konishi et al. 2007). Uniformly sized (2–5 nm), spherical-shaped, and monodispersed mercury nanoparticles were intracellularly synthesized at conditions of pH 8.0 and lower concentration of mercury by *Enterobacter* sp. cells (Sinha and Khare 2011). An anaerobic (in the absence of oxygen) hyperthermophilic (high temperature loving) microorganism, *Pyrobaculum islandicum*, using hydrogen as the electron donor was capable of reducing several heavy metals like uranium (U(VI)), technetium (Tc(VII)), chromium (Cr(VI)), cobalt (Co(III)), and manganese (Mn(IV)) (Kashefi and Lovley 2000). The sulfate-reducing bacterium, *Desulfovibrio desulfuricans*, and metal ion-reducing bacterium, *S. oneidensis*, were capable of synthesizing palladium (Pd) nanoparticles (Lloyd et al. 1998; Yong et al. 2002; De Windt et al. 2005).

15.3.2 Metal Oxide Nanoparticles

Magnetotactic bacteria have been used for the production of magnetic oxide nanoparticles, and similarly other non-magnetic oxide NPs prepared using microorganisms are summarized in Table 15.9.

Table 15.9 Metal oxide nanoparticles synthesized by microorganisms

Metal oxide NPs	Microorganisms	Shape	Location	References
Fe_3O_4	*Shewanella oneidensis QH-2* *Recombinant AMB-1* *Yeast cells* *WM-1* *HSMV-1*	Rectangular, rhombic, cubo-octohedral, wormhole-like, cubical, bullet shape	Intracellular Extracellular	Huang et al. (2007), Steinitz et al. (2010), Merril et al. (1988), Costa-Coquelard et al. (2008), Blum et al. (1987), and Eapen and George (1997)
$FePO_4$	*Yeast cells*	Nanopowder	Extracellular	Tsai and Frasch (1982)
Fe_2O_3	*Shewanella oneidensis MR-1*	Pseudohexagonal rhombohedral	Intracellular	Shevchenko et al. (1996)
Sb_2O_3	*Saccharomyces cerevisiae*	Spherical	Intracellular	Harris and Bali (2008)
$BaTiO_3$	*Lactobacillus* sp. *Fusarium oxysporum*	Tetragonal spherical	Extracellular	Blaylock et al. (1997) and Gardea-Torresdey et al. (2002)
TiO_2	*Lactobacillus* sp. *Fusarium oxysporum*	Spherical	Extracellular	Haverkamp and Marshall (2009); Anderson et al. (1998)
ZrO_2	*Fusarium oxysporum*	Spherical	Extracellular	Sharma et al. (2007)

Researchers are working on the development of magnetic nanoparticles, due to their unique configuration and properties like superparamagnetic and high coercive force and their application in biological separation and medicinal areas. Magnetic nanoparticles like Fe_3O_4 (magnetite) and Fe_2O_3 (maghemite) are known to be biocompatible. They have been actively tried for targeted cancer treatment (magnetic hyperthermia), stem cell sorting and manipulation, guided drug delivery, gene therapy, DNA analysis, and magnetic resonance imaging (Fan et al. 2009).

Magnetotactic bacteria synthesize intracellular magnetic particles comprising iron oxide, iron sulfides, or both (Bazylinski et al. 1994). There are easy chemical methods available to prepare the magnetic oxide nanoparticles and to differentiate biosynthesized particles from artificially synthesized magnetic particles; they are referred to as bacterial magnetic particles (BacMPs) (Arakaki et al. 2008).

BacMPs, which are aligned in chains within the bacterium, are known to work as biological compass needles to enable the bacterium to migrate along oxygen gradients in aquatic environments, under the influence of the Earth's geomagnetic field (Blakemore 1975). BacMPs can easily be dispersed in aqueous solutions because they are coated by organic membranes mainly consisting of phospholipids and proteins. Furthermore, it is found that an individual BacMP contains a single magnetic domain giving superior magnetic properties (Thornhill et al. 1995). Enormous number and variety of uncultured magnetotactic bacteria have been found in various aquatic and other environments since 2000 (Lefèvre CT et al. 2010). Such magnetotactic bacteria bring in novel and innovative methods of obtaining eco-friendly nanoparticles for use especially in the field of biomedicine and other applications.

A low-cost, green, and reproducible method of biosynthesis of Sb_2O_3 nanoparticles mediated by *Saccharomyces cerevisiae* at room temperature has been described (Jha et al. 2009). The synthesized nanoparticles were spherical and aggregated and found to be 2–10 nm in size. SiO_2 and TiO_2 nanoparticles were synthesized from aqueous composites Si and Ti using the fungus *Fusarium oxysporum* (Bansal et al. 2005). $BaTiO_3$ in the form of tetragons with size of 4–5 nm and ZrO_2 in the form of partially spherical nanoparticles with size of 3–11 nm, respectively, were synthesized using *F. oxysporum* (Bansal et al. 2006).

15.3.3 Sulfide Nanoparticles

Sulfide nanoparticles of Cd, Pb, Fe, Zn, and Mo have been synthesized by a variety of microbes with well-defined nanocrystal structure and size both intracellularly and extracellularly. The ability of *Clostridium thermoaceticum* to synthesize CdS both extracellularly and intracellularly using $CdCl_2$ in the presence of cysteine hydrochloride in the growth medium and using the sulfide in cysteine as a source has been reported by Cunningham and Lundie (1993). Extracellular synthesis of CdS with particle size of 20–200 nm using *Klebsiella pneumoniae* exposed to Cd^{2+} ions in the growth medium has been reported (Holmes et al. 1997). CdS nanoparticles have been synthesized intracellularly using yeasts *S. pombe* and *C. glabrata* with cadmium salt solution (Dameron et al. 1989). ZnS and PbS nanoparticles have been successfully synthesized by various microorganisms. Intracellular synthesis of ZnS nanoparticles with a size of 8 nm and 2–5 average diameter has been obtained using *Rhodobacter sphaeroides* and *Desulfobacteraceae*, respectively (Bai et al. 2006; Labrenz et al. 2000). PbS nanoparticles whose diameters were controlled by culture time were synthesized using *Rhodobacter sphaeroides* (Bai and Zhang 2009). According to Ahmad et al. (2002), extracellular synthesis of metal sulfide nanoparticles can be made possible by eukaryotic organisms such as fungi. Extracellular synthesis of stable metal sulfide nanoparticles like CdS, ZnS, PbS, and MoS_2 occur using the fungus *F. oxysporum* on exposure to aqueous metal sulfate solution. The enzymatic reduction of sulfate ions to sulfide ions results in the reaction of Cd^{2+} ions with sulfide ions which ultimately forms quantum dots. Bazylinski et al. (1995) reported the formation of Fe_3S_4 nanoparticles by uncultured magnetotactic bacteria and reported a sedimented sample containing a few magnetotactic bacteria per cm^3 and approximately 10^5 cells after purification. Uncultured cells showed elongated rectangular-shaped magnetosomes numbering nearly 40 and were located within the cells as a cluster. Besides the large cluster, the magnetosomes were aligned forming a chainlike structure. Magnetic FeS nanoparticles were synthesized from sulfate-reducing bacteria (Watson et al. 1999).

15.3.4 Other Nanoparticles

Several organic and inorganic composites with controlled structures have been synthesized using biopolymers such as protein and cells of microbes. $PbCO_3$, $CdCO_3$, $SrCO_3$, PHB, $Zn_3(PO_4)_2$, and CdSe nanoparticles have been synthesized by microbes (Sanyal et al. 2005; Pandian et al. 2009). $SrCO_3$ crystals were synthesized when using the fungus *Fusarium oxysporum* with aqueous Sr^{2+} ions. The proteins secreted during the growth of the fungus were found to be responsible for modulating the morphological structure of strontianite crystals and directing them to higher-order superstructures (Rautaray et al. 2004). Zinc phosphate nanopowders with butterfly-like structure, width ranging from 10 to 80 nm and length 80 to 200 nm, were synthesized using yeasts as biotemplates (Yan et al. 2009). CdSe quantum dots with high luminescence can be synthesized by *F. oxysporum* at room temperature (Kumar et al. 2007).

15.4 Typical Method of Preparation of Nanoparticles from Microorganisms

The required microorganisms are purchased and are aseptically inoculated using growth medium. For example, CDB (Czapek Dox Broth) is used as growth medium for fungi and nutrient broth for bacteria. Growth medium was prepared, autoclaved at 121 °C for 20–30 min, allowed to cool, and inoculated followed by incubation at 30–35 °C with agitation using orbital shaker (180–400 rpm for 24–72 h). It was then centrifuged at 5000–15,000 rpm for 10–30 min and filtered, and the filtrate was used for synthesis of nanoparticles. Precursor salt was treated with the culture filtrate and incubated at 30–35 °C with agitation using orbital shaker (180–400 rpm) for 24–72 h. The nanoparticles were then characterized for various properties.

15.4.1 Mechanism of Nanoparticle Formation by Microorganisms

Intracellular formation of gold and silver nanoparticles by *Verticillium* sp. or algal biomass and their exact mechanism was not fully understood. The formation of nanoparticles occurred on the surface of the mycelia and not in the solution was supported by the hypothesis that the gold or silver ions were trapped first on the fungal cell surface via electrostatic interaction between the ions and negatively charged cell wall from the carboxylate groups in the enzymes. This was followed by the enzymatic reduction of metal ions to form gold or silver nuclei and subsequent reduction and increase of nanoparticles. The nitrate reductase enzyme involved in the synthesis of silver nanoparticles in *B. licheniformis* is induced by nitrate ions and reduces silver ions to metallic silver. The proposed mechanism was that the electron shuttle enzymatic metal reduction process might be responsible for the reduction of silver ions (Kalishwaralal et al. 2008). Biosynthesis of metal nanoparticles requires the cofactor NADH and NADH-dependent nitrate reductase enzyme. The cofactor NADH and NADH-dependent enzymes, especially nitrate reductase secreted by the bacterium *B. licheniformis*, might be responsible for the bioreduction of Ag^+ to Ag^0 and the subsequent results in the synthesis of silver nanoparticles. Synthesis of heavy metal nanoparticles might be due to the genetic and proteomic responses of the microorganisms to toxic environments (Reith et al. 2007). Heavy metal ions such as Hg^{2+}, Cd^{2+}, Ag^+, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} cause severe toxic effects to the survival of microorganisms for which they develop certain genetic and proteomic responses to firmly regulate metal homeostasis (Nies 1999). Numerous metal resistance gene clusters have been docked by microorganisms which enable detoxification of cells using a number of mechanisms like complication, efflux, or reductive precipitation. Hence, metallophilic bacteria thrive in extreme environments such as high concentrations of mobile heavy metal ions, mine waste rock piles, efflux streams of metal processing plants, and naturally mineralized zones (Mergeay et al. 2003).

15.5 In Vivo Synthesis of Nanoparticles in Plants as Bioreactors

Different physical and chemical processes used are usually not cost-effective and labour intensive and are hazardous to the environment and living matter. During the recent years, it has been shown that many biological systems, including plants and algae (Govindaraju et al. 2008), diatoms, bacteria (Lengke et al. 2007), yeast (Kowshik et al. 2002), fungi (Rautaray et al. 2003), and human cells (Anshup et al. 2005), convert inorganic metal ions into metal nanoparticles through the reductive materials of the metabolites present in these organisms.

It is well known that plants are capable of reducing metal ions both on their surface and in various parts and tissues. Plants, having very high metal ion accumulation and reductive capacity, are tried for extracting precious metals from land which would be economically justifiable; this approach is called phytomining. The metals accumulated by the plants can be recovered further through sintering and other methods.

It has been shown that plants can accumulate metals from the soil in which they are grown. The plants which can accumulate a metal to 1000 times the highest concentration found in normal accumulator plants are termed as ‘hyperaccumulators’ (Kumar et al. 1995). There are several evidences that support the formation of gold and silver nanoparticles in living plants (Gardea-Torresdey et al. 2002, 2005).

Studies of the plants have shown that metals are usually deposited in the form of nanoparticles. For example, *Brassica juncea* (mustard greens) and *Medicago sativa* (alfalfa) can accumulate 50 nm silver nanoparticles up to 13.6% of its own weight when they were grown using silver nitrate solution (Gardea-Torresdey et al. 2002). In addition, gold NPs with a size of 4 nm were seen in *M. sativa* (Harris and Bali 2008) and semi-spherical copper particles with a size of 2 nm in *Iris pseudacorus* (yellow iris) when they were grown on substrates containing salts of the respective metals.

There are certain limitations when industrial application of this technology is considered. The size and shape of nanoparticles with this technology vary depending on their localization in the plant, due to the difference in metal ions content and the movement of nanoparticles in various tissues of the plant parts. These factors may also influence the level of metal deposition and also the development of new nucleation and propagation of nanoparticles. The differences in the size and morphology of nanoparticles formed in plants may reduce their use in applications when specific and finely tuned sizes and shapes are required. This shows the inability of the plant-synthesized nanoparticles to suit the market requirements. Further, isolation, extraction, and purification of nanoparticles from plant materials involve complicated procedures, with low recovery.

However, Makaraov et al. (2014) have reviewed the most important advantages of the use of plants as bioreactors for producing nanoparticles over the other biological systems. They have mentioned that the low cultivation cost, less production time, safety, and the ability to high production quantities suggest plants as attractive sources for nanoparticle synthesis.

15.5.1 In Vivo Synthesis of Nanoparticles in Live Plants

Bali et al. (2006) had described a cost-effective technique for the synthesis of metallic nanoparticles inside live plants. Nanoparticles of common heavy metal ions, such as Ag, Cu, Co, Zn, and Ni, were synthesized by exposing plants to aqueous metal salt solutions. These experiments were used to determine the importance of three plant species *Brassica juncea*, *Helianthus annuus*, and *Medicago sativa* for producing nanoparticles. The influence of parameters such as exposure time, substrate metal ion concentration, and chelating agent addition were all investigated. *Brassica juncea* was found to be the best plant for extracting metals from aqueous solutions and depositing them as intracellular nanoparticles. It has been shown in their experiments that silver was accumulated most readily, up to 9.2% on a dry weight basis in the case of *Brassica juncea*. Cobalt was the least extracted (to a maximum of 1.5% by weight). Luca Marchiol et al. (2014) studied the in vivo formation of silver nanoparticles (AgNPs) in *Brassica juncea*, *Festuca rubra*, and *Medicago sativa*. Plants were grown in Hoagland's solution (plant nutrient) for 30 days and then exposed for 24 h to a solution of 1000 ppm $AgNO_3$. The content of reducing chemicals such as glucose, fructose, ascorbic acid, citric acid, and total polyphenols was determined in the leaf extracts of control plants. Ag content in plant fractions was determined by inductively coupled plasma atomic emission spectroscopy. Despite the short exposure time, the Ag uptake and transmission to plant leaves were very high, i.e. 6156 and 2459 mg kg^{-1} in *B. juncea* and *F. rubra*, respectively.

Figure 15.9 shows the silver Nps in the leaves of *Brassica juncea* (Marchiol et al. 2014).

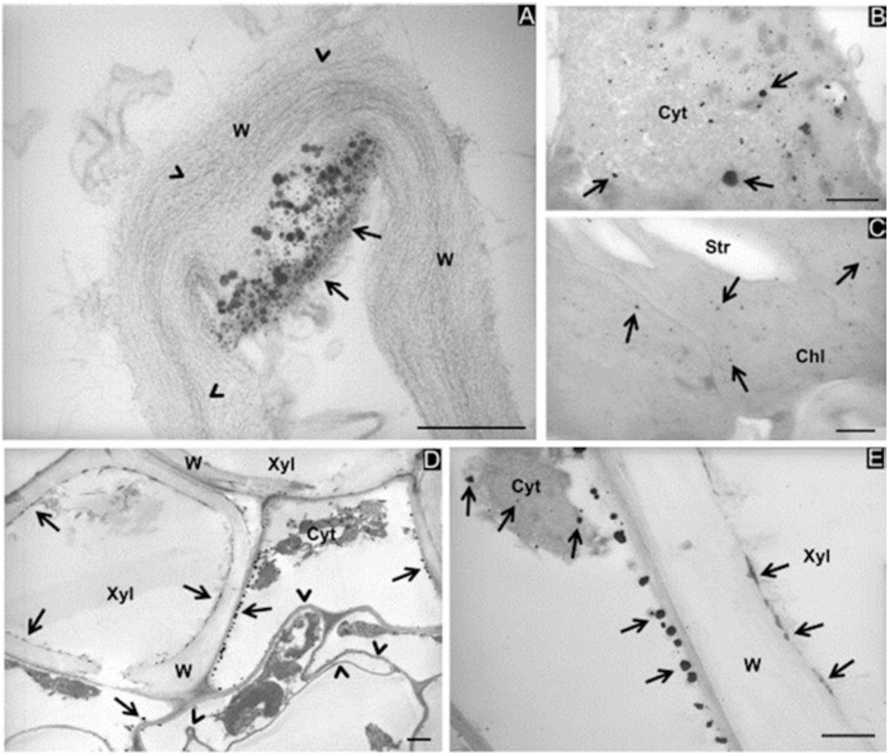


Fig. 15.9 Ag particles in the leaves of *Brassica juncea* (Marchiol et al. 2014)

Nps of different sizes are also visible in the parenchymal cells as shown in Fig. 15.10a–c of the leaves of the plants. They are present in the inner side of cell walls, in cytoplasm and in the chloroplasts. The wall architecture was found to be modified, showing uncompacted microfibrils. In (d), a xylem vessel (Xyl) contains numerous Nps along the cell wall. In (e), the surrounding cells show also numerous Nps, along the plasmalemma and in the condensed cytoplasm. Bars correspond to 250 nm in (a, b, c), 1000 nm in (d), and 500 nm in (e).

The TEM images (Figs. 15.10 and 15.11) confirm the presence of AgNPs through all of the formed plant tissues of the species, in the form of single particles and/or intracellular clusters of different sizes and shapes. This fact suggests that after entering through the root, AgNPs are able to move to remote positions and form aggregates throughout the plants. This movement of Ag Nps may occur through the vascular system, but it is not very clear whether Nps are transported as nanosized individuals or as aggregates. TEM observations also show ultrastructural changes in different cell compartments along with nanoparticle aggregates. Probably, plant cells respond to the formation of a high density of nanoparticles by changing their subcellular organization. The main changes occur in cell membranes, viz. plasmalemma, tonoplast, and chloroplast thylakoids, as Ag is able to inhibit many enzymes,

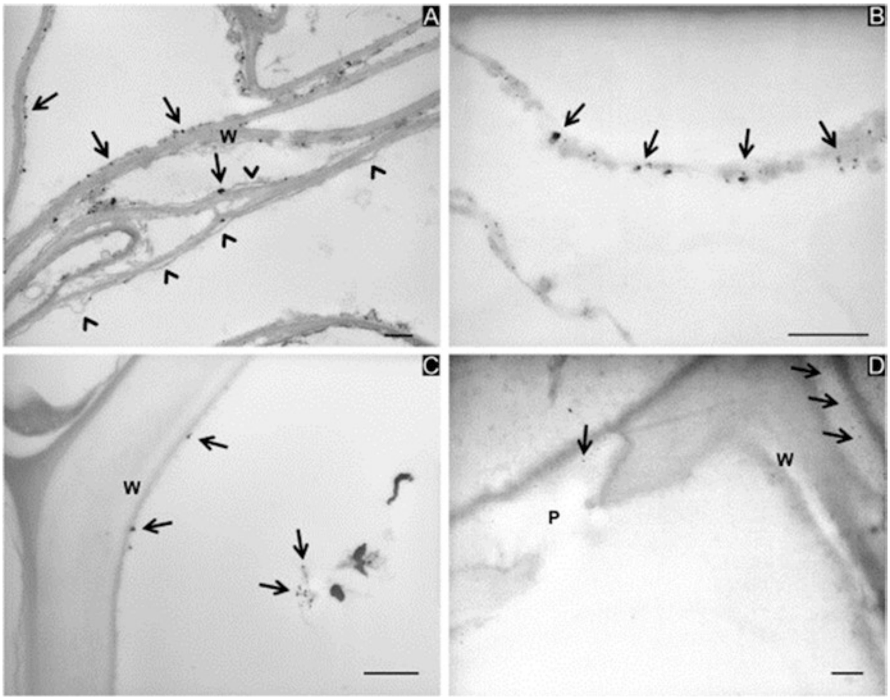


Fig. 15.10 Ag particles in the roots of *Festuca rubra* (**a**) and *Medicago sativa* (**b–d**). Electron-dense Ag spots are seen on the plasmalemma of the cortical parenchymal cells (Marchiol et al. 2014)

especially those containing sulfhydryl groups, thereby altering membrane permeability (Koontz and Berle 1980).

They have also observed that the ultrastructural changes were different in the diverse plant organs. Even though the ICP analyses showed a higher metal concentration in the root tissues of plants, the aerial leaf fractions were more damaged by $AgNO_3$ treatment than the roots. The less toxic effects observed in the root tissue may be due to the ability of the plants to 'block' and store AgNPs at the membrane level. On the other hand, nanosized particles located to the upper levels of the plant resulted in a higher toxicity, which was also reported for other metal-based nanoparticles (Aubert et al. 2012). To supplement these observations, AgNP synthesis in living plants has also been demonstrated previously in *B. juncea* and *M. sativa* in hydroponics by Harris and Bali (2008), Haverkamp and Marshall (2009), and Beattie and Haverkamp (2011).

Similarly, Starnes et al. (2010) detected the formation of AuNPs in *M. sativa* and other species as early as 6 h after the start of exposure to $KAuCl_4$. It was also verified that plant growth conditions have an effect on metal NP synthesis variations in temperature, pH, and photosynthetically active radiation (PAR) which influence the size and shape of growing AuNPs. Theoretically, this suggests the possibility of

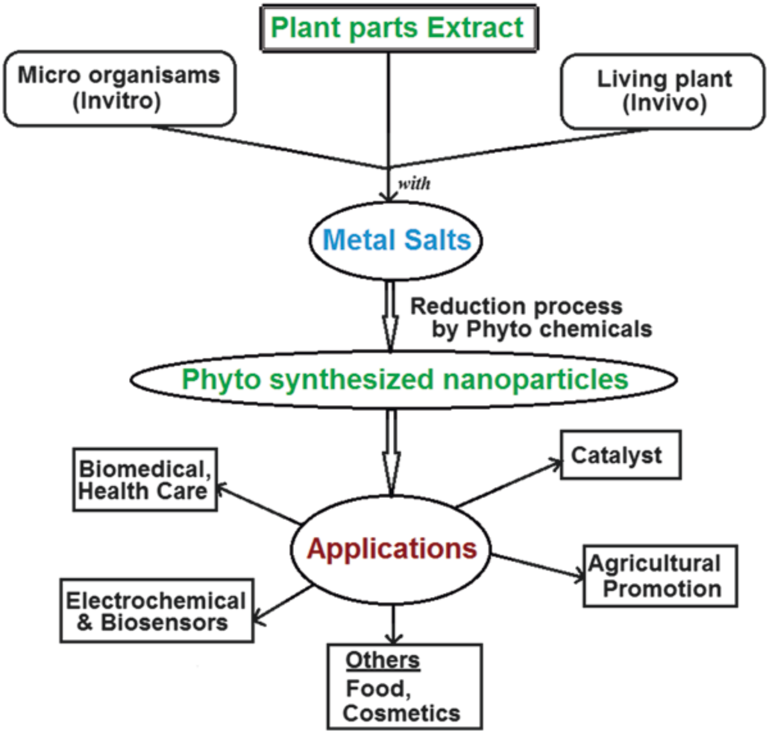


Fig. 15.11 Phytoengineered nanomaterial and applications

managing living plants as nanofactories and promoting the synthesis of nanomaterials of desired size and shape. The most intriguing question about plant metal NP synthesis is where and how this phenomenon begins. So far, the mechanism of this process in living plants is completely clarified. Wherever this occurs, it is highly likely that the key factor is the presence of immediately available reducing agents.

15.5.2 Mechanism of Formation of NPs in Live Plants

Beattie and Haverkamp (2011) have shown that in the plant *Brassica juncea* chloroplasts are the sites of the high-reducing sugars such as glucose and fructose which are responsible for the conversion of metal salts to Nps. This explains the thinking that plants having the highest concentrations of sugar molecules act as 'nanofactories' for preparation of metal nanoparticles. It is also suggested that in addition to carbohydrates, proteins, flavonoids, and terpenoids of plant cells also are responsible for reduction in the biosynthesis of metal NPs and their stabilization (Park et al. 2011; Gan and Li 2012; Prasad 2014; Tripathi et al. 2016, Shweta et al. 2016). Further, it is suggested that metal NP synthesis starts in healthy cells, which then rapidly undergo growth until they are completely damaged due to its toxicity. Thus, it could be that metal NP synthesis is initiated within the chloroplasts in a healthy cell and ends in the cytoplasm of the same cell, which gets damaged.

It may be accepted now that plants can be exploited for their ability to synthesize metal Nps by in vivo *method*, but furthermore concrete experiments are required in order to understand precisely the mechanism of metal nanoparticle formation as to why differences occur in various plants with respect to different metals, variation in the amount, forms, sizes, and 3D structures of the in vivo-synthesized metal NPs.

15.6 Applications

Nanoparticles have drawn great attention due to their unusual properties and applications advantageous over their bulk counterparts. A number of applications of nanoparticles are being tried in biomedical, health care, food and drinks, sensors, agriculture, paints and coatings, etc. (Fig. 15.11); few applications of nanomaterials are given here.

Tables 15.1, 15.2, 15.3, 15.4, 15.5, 15.6, and 15.7 show the various applications of the metal, metal oxide, sulfide, etc. nanoparticles. Whatever may be the preparation method followed, namely, whether NPs are prepared from plant extract or by microorganisms or in living plants, the application effect need not be different. Phytoengineered NPs are mostly applied as antimicrobial agents, as electrochemical sensors and biosensors, in medicine and health care, and in agricultural crop promotion.

Silver nanoparticles exhibit high bactericidal action against both Gram-positive and Gram-negative bacteria. Electrochemical sensors and biosensors can be exclusively designed and enhanced due to the appropriate physical and chemical properties of nanoparticles. Metal, metal oxide, and semiconductor nanoparticles are being used for development of electrochemical sensors and biosensors, as these nanoparticles play diverse roles in different sensing systems. In addition, these nanoparticles provide the immobilization of biomolecules, the catalysis of electrochemical reactions, the improvement of electron transfer on electrode surfaces and proteins, and the labelling of biomolecules. For example, deoxyribonucleic acid (DNA) can also be immobilized with nanoparticles and used as electrochemical DNA sensors. In order to immobilize DNA onto the surfaces of nanoparticles, the DNA strands are modified with functional groups that can work together powerfully along with nanoparticles.

It is well known that many herbal/medicinal plants are being tried for medical applications long before. Thus, if nanoparticles are synthesized from herbal/medicinal plants, they can be utilized for biomedical applications such as in vivo diagnosis of biomedical disorders. Recently, magnetic iron oxide nanoparticles are being tried in patients for both diagnosis and therapy for more effective medication with less unfavourable side effects. Gold nanoparticles coated with protein antigens are developed and used to have an exclusive and greatly explicit immunoassay system. Phytoengineered nanoparticles are capable of use as efficient drug delivery systems to improve several crucial properties of drugs, such as solubility, in vivo stability, proper biodistribution, etc. Pandey and Khuller (2007) designed nanoparticles for

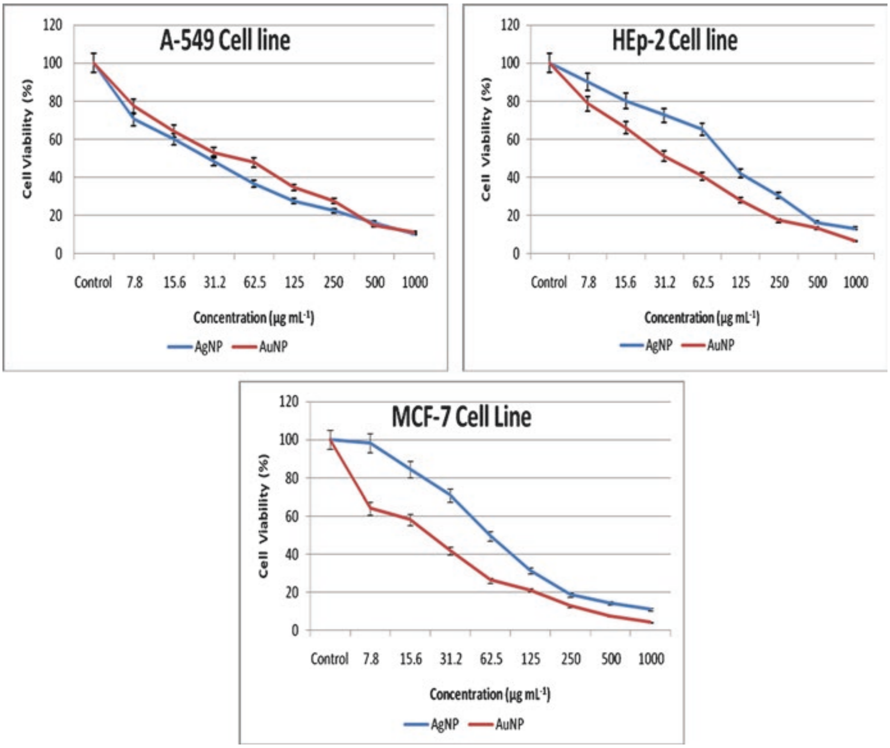


Fig. 15.12 Comparative anticancer efficacy of AgNP and AuNP on A549, HEp-2, and MCF-7 cells

the growth of oral drug delivery system and suggested that nanoencapsulation may be useful for developing an appropriate oral dosage form for streptomycin and for other antibiotics that are not injectable. Elechiguerra et al. (2005) revealed the interaction of metal nanoparticles with viruses and explained that silver nanoparticles experience a size-dependent interaction with HIV-1 with the nanoparticles of 1–10 nm close to the virus. Currently, most of the imaging studies are carried out in cell culture using gold nanoparticles. The cellular imaging of single molecules has also been reported by Peleg et al. (1999), utilizing the advantage of the enhanced second harmonic signal by antibody-conjugated gold nanospheres. The use of nanoparticles in cosmetics and medicine coating is widely increasing day by day. Metal oxide nanoparticles such as zinc oxide and titanium dioxide now emerge in household products, general or assorted cosmetics, sunscreens, toothpaste, and medicine. Herbal plant mediated nanoparticles can be more effective without any side effects in such applications.

Mukundan et al. (2017) have also shown improvement in in vitro anticancer activity of silver and gold nanoparticles on A549, HEp-2, and MCF-7 cells (Fig. 15.12).

Nanosensors and nanosmart delivery systems are finding use in agricultural natural assets like water, nutrients, and chemicals during precision agricultural farming

Table 15.10 Effect of metal nanoparticles in plants

Metal	Plants	Effect	References
Aluminium	Corn, cucumber, lettuce, radish, rapeseed, ryegrass, red kidney beans	Germination, toxicity, root growth	Burris et al. (2012), Doshi et al. (2008), Roghayyeh et al. (2010), Miao et al. (2007), Musante and White (2010), Husen and Mishra (2002), Barrena et al. (2009), and Feng et al. (2013)
Copper	Lettuce, mung bean, wheat, zucchini	Germination, seedling growth, shoot growth, biomass	Lee et al. (2008)
Dodecanethiol functionalized gold	Lettuce	Germination, shoot/root ratio	Shah and Belozerova (2009)
Iron	Flax, meadow fescue, red clove, white clover, barley, ryegrass	Germination, inhibited germination	El-Temsah and Joner (2012)
Mixture of gold/copper and Pd in aluminium hydroxide matrix	Lettuce	Germination, shoot/root ratio	Shah and Belozerova (2009)
Silver	Flax, cucumber, lettuce, clover, wheat, barley, ryegrass, zucchini, onion	Germination, toxicity, biomass, shoot and root length, transpiration, mitosis, metaphase, sticky chromosome, cell wall	El-Temsah and Joner (2012)
Silver colloidal form	Ryegrass, flax, barley	Germination, shoot length	El-Temsah and Joner (2012)

(Prasad et al. 2014). Nanosensors kept in the field can be able to sense the presence of plant viruses and the level of nutrients. Nanoencapsulated fertilizer materials help in reduced fertilizer consumption with less environmental pollution through their slow and sustained release in the soil. To check and improve the quality of agricultural manufacture, nanobarcodes and nanoprocessing are also used. Li et al. (2012) have used the idea of barcodes for economical, rapid, and effortless decoding for recognition of diseases. They have created probes or nanobarcodes which may tag multiple pathogens in a farm, and these can be easily detected using any fluorescent-based tools. Scientists have also studied and developed nanosensors which can interact with auxin that is important for root growth and seedling organization and to regulate the plant growth.

Tables 15.10 and 15.11 give the application of metal and metal oxide nanoparticles, particularly in agriculture for promotion of germination and root and shoot growth.

Table 15.11 Effect of metal oxide nanoparticles in plants

Metal	Plants	Effect	References
Al_2O_3	Corn, cucumber, lettuce, radish, rapeseed, ryegrass, carrot, cabbage, maize	Germination, root growth	Yang and Watts (2005)
CeO_2	Alfalfa, tomato, cucumber, maize, soybean, wheat, coriander, rice	Shoot growth, biomass, germination, root and stem growth, catalase activity, ascorbate peroxidase activity, H_2O_2 generation, electrolyte leakage, lipid peroxidation	Lopez-Moreno et al. (2010), Wild and Jones (2009), Morales et al. (2013), and Rico et al. (2013)
Fe_3O_4	Pumpkin, cucumber, lettuce	Toxicity	Zhu et al. (2008)
Magnetite (iron oxide)	Soybean	Chlorophyll levels	Ghafariyan et al. (2013)
Silica/titanium dioxide	Soybean	Germination, shoot growth, absorption and use of water and fertilizer	Lu et al. (2002)
$Ni(OH)_2$	Mesquite	No effect	Parsons et al. (2010)
Nanosized TiO_2	Wheat	Germination, shoot and seedling, root dry matter production	Feizi et al. (2012)
Nanoanatase (TiO_2)	Spinach	Rubisco activase, Rubisco carboxylation, photosynthetic carbon, N_2 fixation, light absorbance, carbon di oxide assimilation	Gao et al. (2006), Yang et al. (2007), and Linglan et al. (2008)
TiO_2/inorganic bentonite clay	Maize	Hydraulic conductivity, growth, and transpiration	Asli and Neumann (2009)
ZnO	Soy bean, ryegrass, corn, cucumber, lettuce, radish, rapeseed, zucchini	Root growth, biomass, shrank root tips, collapsed cortical cells, germination, root growth and elongation	Lopez-Moreno et al. (2010)
3-Amino-functionalized SiO_2	Lettuce	Germination, shoot/root ratio	Shah and Belozerova (2009)

Nanocapsules are also tried for introduction of herbicides through cuticles and tissues to permit slow and sustained release of the active substances. This acts as ‘magic bullets’, containing herbicides, chemicals, or genes which target plant parts to liberate their substance. 3 nm mesoporous silica nanoparticle has been tried in delivering DNA and chemicals into isolated plant cells. Mesoporous silica nanoparticle are chemically coated, and they act as containers for the genes delivered into the plants and can trigger the plant to take the particles through the cell walls in a controlled way, without any harmful side effects. This technique firstly has been applied to establish DNA fruitfully to tobacco and corn plants.

15.7 Conclusions

In contrast to the conventional chemical methods, plant-mediated methods are being tried by various researchers to synthesize nanoparticles of metal, metal oxides, and other materials with different size, shape, and quantity. These plant-mediated methods include synthesis of these NPS by using different parts of plants, in vitro synthesis using bacteria, fungi, yeast, algae, etc. and in vivo synthesis using phytomining and bioaccumulation of NPs in live plants. These NPs are explored for various applications as potent antimicrobial agents, as electrochemical sensors and biosensors, in medicine and health care, in agriculture and crop biotechnology, and as pests, nutrients, plant hormones, etc. and for their in vitro anticancer efficiency.

While the mechanism of formation of NPs is somewhat clear in the in vitro synthesis methods, the mechanism of formation of NPs in live plants is not well established.

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Plants and Carbon Nanotubes (CNTs) Interface: Present Status and Future Prospects

16

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Abstract

The unique characteristics of nanomaterials utilizing carbon have drawn great attention and interest since the breakthrough of fullerenes (in 1985), carbon nanotubes (CNTs, in 1991), and graphene (in 2004). This discovery has led to the promotion of developing methods in order to produce it at large industrial scales. Engineered nanomaterials are continuously finding its applications in medical sector, technical devices, environmental purposes, as well as agricultural sector. Despite its wide applications, there is also the unintended release of carbon-based nanostructures into the environment, thereby affecting or posing inimical

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effect toward the living systems like plants. The researchers are trying to engineer such nanoparticles in a way that it may impose some advanced and beneficial applications in living systems. One of the engineered carbon-based nanomaterials includes carbon nanotubes (CNTs) which can be further classified as single-walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs), water-soluble multiwalled carbon nanotubes, functionalized single-walled carbon nanotubes, double-walled carbon nanotubes etc. This chapter, therefore, focuses on all aforementioned types of carbon nanotubes, techniques utilized in synthesis, and current status of research with respect to the impact of carbon nanotubes on plant growth and development addressing relevant knowledge gap.

Keywords
Carbon nanotubes • Plants • Uptake • Translocation • Nanotechnology

16.1 Introduction

Nanotechnology and nanoscience are the science that includes the study of any particle at nanoscale level which ranges from 1 to 100 nm (Nagarjan 2008; Ju-Nam and Lead 2008; Suman et al. 2010). Moreover, the particles falling in the range of 1–100 nm are known as nanoparticles (Buzea et al. 2007). Despite their small sizes, they are being used in agriculture (Sabir et al. 2014; Parisi et al. 2015; Prasad et al. 2017a), wastewater treatment (Nassar 2013; Esakkimuthu et al. 2014; Aziz et al. 2015), drug delivery (Silva et al. 2014; Prasad et al. 2017b), electronics (Millstone et al. 2010), medicines (Shi et al. 2010; Aziz et al. 2016), etc. (Fig. 16.1). Due to the vast applications of nanoparticles in daily life, its production also increases day by day. This increasing production of nanoparticles should be analyzed in order to know whether they may be harmful for ecosystem or not because many nanoparticles possess potential to cause pollution when they interact or come in contact with atmospheric gases and living organisms (Conway et al. 2015; Tripathi et al. 2017a). The pollution created from nanoparticles in the environment is known as nanopollution (Gao et al. 2015). Plants are considered as the main part of the food web, they are under the risk of nanoparticle exposure either through soils (by using nanopesticides), atmospheric deposition, or runoff (Gottschalk and Nowack 2011; Conway et al. 2015; Tripathi et al. 2017a, b, c). A nanoparticle comes in the environment by natural processes or can be manufactured by various physical, chemical, and biological methods (Ingale and Chaudhari 2013; Iravani et al. 2014; Prasad et al. 2016), there are few examples of natural nanoparticles are dust storms, fires, volcanoes, etc. (Buzea et al. 2007; Strambeanu et al. 2015), and manufactured nanoparticles include carbon nanotubes (Eatemadi et al. 2014; Lee et al. 2016), copper oxide nanoparticles (Umer et al. 2012), etc. However, there are different functions of nanoparticles according to their size, shape, concentrations etc. from which they perform either beneficial impact or inimical impact on plants and living organisms (Tables 16.1 and 16.2; Fig. 16.2) (Ma et al. 2010; Tripathi et al. 2017a, b, c). Among

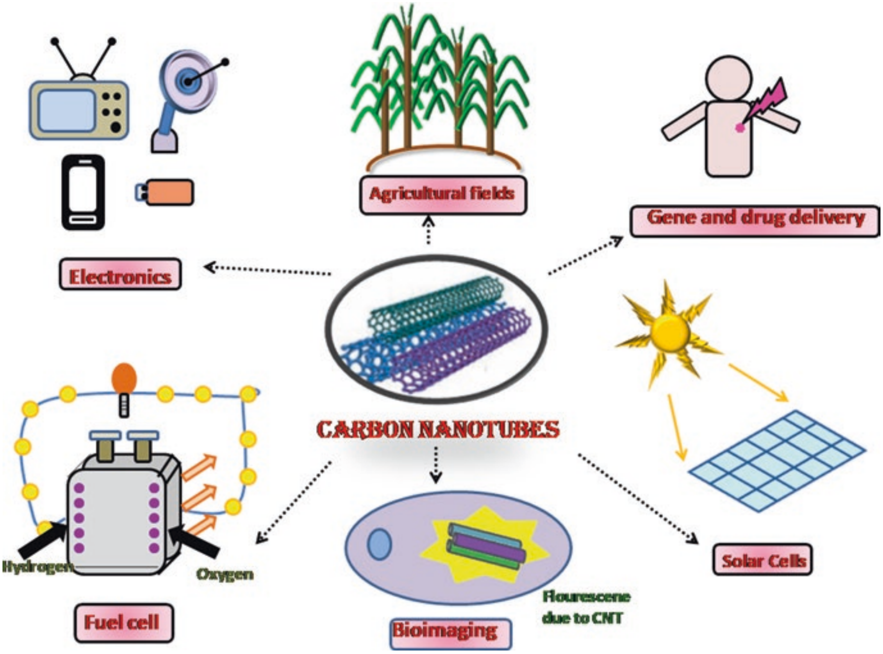

Fig. 16.1 Applications of carbon nanotubes in various sectors

all the nanoparticles, carbon nanotubes are fetching more attention due to their attractive structure, shape, size and unique physical, chemical, and biological properties (Chen et al. 2003; Kam et al. 2004; Cherukuri et al. 2004; Bianco et al. 2005; Serag et al. 2015). Carbon nanotubes are actually engineered nanoparticles whose synthesis evolved in 1985, after the discovery of Buckminster (C_{60}) fullerenes (Bergmann and Machado 2015; Hong et al. 2015; Mukherjee et al. 2016). Major classification of carbon nanotubes includes single-walled carbon nanotubes, multi-walled carbon nanotubes, fullerene, cup-stacked carbon nanotubes etc. (Serag et al. 2015). Its structure is very unique; they are engineered by folding the sheets of graphene (Iijima 1991; Dai 2002; Golberg et al. 2008; Serag et al. 2015). Its major applications occur in biological and medicinal field involving tissue engineering, drug and gene delivery and in many diagnostic areas (Panyam and Labhasetwar 2003; Zanello et al. 2006; Harrison and Atala 2007; Rao and Srivastava 2014; Prasad et al. 2016). Other than this, they are also being used in batteries, biosensors, microelectronics, and energy storages (Lee et al. 2015). Hence, there is maximum chance of interaction of nanoparticles with plants due to their extensive applications in many fields (including research) and rapidly increasing production (Fig. 16.1) (Pitsillides et al. 2003; Rao and Srivastava 2014). This also led to advances in agricultural sectors, by shaping the modern approaches in agriculture (Rao and Srivastava 2014; Sangeetha et al. 2017). Carbon nanotubes are also widely used because they can be easily penetrated in the cell wall of any plant and hence can be effectively used in agriculture by acting as direct delivery system for many fertilizers and pesticides (Rao and Srivastava 2014). Although in the field of life science,

Table 16.1 Beneficial impact of carbon nanotubes on different plants at various concentrations

Type of carbon nanotube	Size (nm)	Concentration(s)	Plant(s)	Beneficial effects	Reference(s)
MWCNTs	–	40 µg/ml	*Lycopersicum esculentum*	Increased percentage of seed germination and seedling growth	Morla et al. (2011)
	10 nm	75 wt%	*Medicago sativa*, *Triticum aestivum*	Enhanced elongation of roots and seedling growth	Miralles et al. (2012)
	Not available	25–100 µg/mL	*Hordeum vulgare*, *Glycine max*, *Zea mays*	Increased germination and growth, hence overall biomass of the plant; increased root length in *Glycine max*	Lahiani et al. (2013)
	25 nm	20, 50 mg/L	Wheat, maize, peanut, garlic	Elongated length of roots and shoots	Khodakovskaya et al. (2013)
	25	5 up to 500 µg/mL	*Nicotiana tabacum*	Flowering and fruiting increased twice as compared to control	Khodakovskaya et al. (2012)
	10–35	50 and 200 µg/mL	*Lycopersicon esculentum*	Increased overall biomass content, upregulation of stress-related genes, and penetration of MWCNTs into roots, leaves, and fruits	Khodakovskaya et al. (2011)
	Not reported	10, 20, 40 mg/L	*Lycopersicon esculentum*	Enhanced moisture contents in seed and improved rate of germination	Khodakovskaya et al. (2009)
	110–170	20 µg/mL	*Brassica juncea* and *Phaseolus mungo*	Increased root growth	Ghodake et al. (2010)
	~30	2.3 × 10^{-3} mg/mL	*Brassica juncea*	Improved germination and seedling growth	Mondal et al. (2011)
	< 50	25, 50, 100, 250, 500 mg/L	*Satureja*	Increased callus growth	Ghorbanpour and Hadian (2015)
	6–13	10–50 mg/L	*Zea mays*	Stimulated growth	Zhai et al. (2015)

MWCNTs, double-multiwalled carbon nanotubes	6–9	40 µg/mL	*Lycopersicon esculentum*	Increased growth, biomass, and concentration of nutrient elements	Tiwari et al. (2013)
WS-CNT	10–30	6.0 µg/mL	*Cicer arietinum*	Increased growth rate	Tripathi et al. (2011)
Pristine MWCNTs, double-multiwalled carbon nanotubes	6–9	20 mg/L	*Zea mays*	Improved water absorption, biomass of plant, and concentration of essential nutrients like Ca and Fe	Tiwari et al. (2014)
COOH- MWCNTs	10–20	50 µg/mL	*Triticum aestivum*, *Zea mays*, *Arachis hypogaea*, and *Allium sativum*	Increased root, shoot, and biomass	Rao and Srivastava (2014)
SWCNTs-COOH, SWCNTs-Fe	1.0–2.0, 3.5–4.0	4 µg/ml	*Rubus adenotrichos*	Elongated roots and shoots	Flores et al. (2014)
				Enhanced cell metabolism	
SWCNT, fSWCNT	3	9, 56, 315, and 1750 mg/L	*Allium cepa*, *Cucumis sativus*	Enhanced elongation of roots	Cañas et al. (2008)
SWCNTs	8–15	10–40 mg/L	*Lycopersicum esculentum*, *Allium cepa*	Enhanced the rate of germination	Haghighi and da Silva (2014)
	0.86–2.22	50 mg/L	Tomato	Increased fresh and dry plant biomass	Khodakovskaya et al. (2011)
CNTs	8	50, 100, 150 mg/L	*Oryza sativa*	Improved rate of germination	Jiang et al. (2014)

Table 16.2 Negative or no any significant impact of carbon nanotubes on different plants at various concentrations

Type of carbon nanotube	Size (nm)	Concentration(s)	Plant(s)	Negative effects	Reference(s)
MWCNTs	10–30	20, 40 mg/L	*Oryza sativa*	Condensed chromatin, detachment of cell membrane from cell wall, generation of ROS, and decreased cell viability, ultimately cell death	Tan et al. (2009)
	9.5	10, 60, 100, 600 mg/L	*Arabidopsis*	Reduced cell viabilities and dry weight, cell chlorophyll content, and superoxide dismutase activities	Lin et al. (2009a, b)
	–	10–50 mg/L	Soybean	Reduced growth, uptake, and translocation	Zhai et al. (2015)
	10–150	1000 mg/L	Wheat, rapeseed	No effect on development	Larue et al. (2012)
	~11	500, 1000 mg/L	*Amaranthus tricolor*	Red pigment of leaf removed, necrosis, curling, and wilting also seen in the treated leaf. Concentration-dependent reduction in root-shoot height, root-shoot weight, and leaf numbers. Enhanced electrolytic damage and generation of ROS Increased apoptosis	Begum and Fugetsu (2012)
	10	10 ppm	*Cichorium intybus*	Reduced germination percentage	Pilevar et al. (2015)
	13–16	1000 mg/L	*Zucchini*	Reduced biomass but seed germination unaffected	Stampoulis et al. (2009)
	10–20	2000 mg/L	*Lettuce*	Declined root length but no effect on germination of seeds	Lin and Xing (2007)
	110–170	100 mg/L	*Triticum aestivum*	No significant effect on growth of roots or shoots	Wild and Jones (2009)
	3 ± 4	40–2560 mg/L	*Alfalfa*, *wheat*	No effect on seed germination	Miralles et al., (2012)
	110–170	10, 20, 40 mg/L	*Mustard*, *black lentil*	No effect on seed germination	Ghodake et al., (2010)
	Not reported	100 mg/L	*Barley*, *maize*, *soybean*	No effect on seed germination	Lahiani et al., (2013)

	20	50 and 200 µg/mL	*Lycopersicon esculentum*	Elevated expression of *CycB* gene and hence plant cell divisions and growth	Khodakovskaya et al. (2013)
	7–15	5, 20, 50 mg/L	*Allium cepa*	DNA damage	Ghosh et al. (2015)
	Not reported	5 and 10 mg/L	*Allium cepa*	DNA damage	Ghosh et al. (2011)
O-MWCNTs	6–13	10, 20, 40, 80, 160 mg/L	*Triticum aestivum*	No effect on seed germination	Wang et al. (2012)
SWCNTs	8–15	10–40 mg/L	*Raphanus sativus*, *Brassica rapa*	Showed toxicity by decreasing germination rate	Haghighi and da Silva (2014)
	1.19 (major), 18, 722	400 mg/L	*Oryza sativa*	Delayed flowering, declined yield	Lin et al. (2009a, b)
	8	104, 315, 1750 mg/L	*Lycopersicum esculentum*	Reduced root length	Cañas et al. (2008)
	8	104, 315, 1750 mg/L	Cabbage, carrot, lettuce	No significant length	Cañas et al. (2008)
	1–2	20 mg/L	Maize	No any effect on germination of seeds	Yan et al. (2013)
	1–2	5–250 mg/L	*Arabidopsis*, *Oryza sativa*	Cell aggregation, condensation of chromatins, plasma membrane deposition, H_2O_2 accumulation	Shen et al. (2010)
fCNTs	8	104, 315, 1750 mg/L	*Lettuce*	Reduced length of roots	Cañas et al. (2008)
fSWCNTs	8	9, 56, 315, 1750 mg/L	*Cabbage*, *carrot*, *lettuce*, *onion*, *tomato*	No effect on development	Cañas et al. (2008)
CNTs	Not reported	Not reported	*Arabidopsis*	Declined rate of photosynthesis and transpiration. Reduced carbon gain and chlorophyll fluorescence	Voleti and Wait (2014)

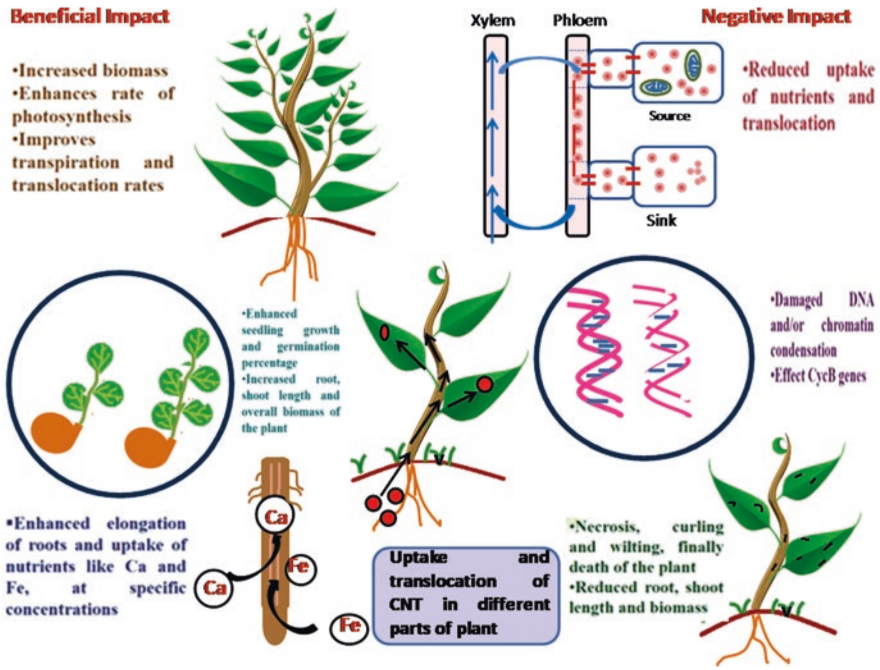

Fig. 16.2 Impact of carbon nanotubes on plants

most of the researches were performed on humans and animals, but some studies revealed the impact of carbon nanotubes on plants, especially on morphological or physiological developments because plants are thought to be geo-physico-chemical transducers. They are very necessary for life since they are the only source of oxygen and food supply and also help in sustaining life (Donaldson et al. 2006; Martinelli et al. 2012; Tiwari et al. 2013). Plants are the last receiver of carbon nanotube contamination involved or present in the environment. Hence, carbon nanotube nanoparticle-plant interaction must be assessed thoroughly from cell to organism level (Tiwari et al. 2013). From this study of interaction, one can also develop the nanoagricultural technologies, which include the area of nanobiotechnology and help in improving the biomass of the plants (Srinivasan and Saraswathi 2010). On the other hand, the toxicity of carbon nanotubes in plants is also not negligible. They exhibit high tendency to accumulate in plants and their cells (Khodakovskaya et al. 2009; Liu et al. 2009a; Begum et al. 2012). Many studies revealed the toxicity of carbon nanotubes in plants (Yang and Watts 2005; Lin and Xing et al. 2007; Tan et al. 2009; Lin et al. 2009a, b; Begum and Fugetsu 2012), and after penetration of carbon nanotubes in plants, they follow a pathway link through which carbon nanotubes enter in the biological cycles and food chain (Wierzbicka and Antosiewicz 1993; Begum and Fugetsu 2012). In addition to this, Tan and Fugetsu (2007) and Cañas et al. (2008) also reported the inimical impact of carbon nanotubes by reduced seed germination and inhibited growth percentage in selected plants and their cells (Fig. 16.2). Primary criteria by which carbon nanotubes inhibit or alter the growth of plants include generation of ROS and oxidative stress (Tan et al. 2009, Begum et al. 2011; Begum and Fugetsu 2012). The generation of ROS and oxidative stresses causes the damaging effects on other parts or organelles of plants like mitochondria, cell membrane, DNA etc. (Apel and Hirt 2004), which ultimately cause effect on reproduction, development, and viability of organisms (Begum and Fugetsu 2012).

16.2 Properties, Synthesis, and Classification of Carbon Nanotubes

16.2.1 Properties

Carbon is the essential element having atomic number six with six electrons in their shell and electronic configuration $1s^2$, $2s^2$, $2p^2$. Moreover, discoveries revealed that similar sp^2 configurations were also found in carbon nanotubes (Chico et al. 1996), graphene (Ouyang et al. 2001), and fullerenes (Kim et al. 2003) (Eatemadi et al. 2014). Carbon nanotubes are carbon allotropes having cylindrical structures with length to diameter ratios up to 132,000,000:1 (Wang et al. 2009a). Carbon nanotubes are found in various structures like armchair, zigzag etc. Carbon nanotubes that are found in armchair tubelike structure, their diameter is found to be 1.2 nm, while their carbon bond length reported is around 1.42 Å (Ganesh 2013). Furthermore, their lattice energy, overlap energy, and density were reported to be around 17 Å, 2.5 eV, and 1.40 g/cm^3 respectively (Ganesh 2013). In addition to this, their thermal conductance and resistivity at 300 K were around 1/12.9 kW^{-1}, respectively (Ganesh 2013).

16.2.2 Synthesis of CNTs

There are a number of methods given by researchers by which carbon nanotubes can be synthesized. Some of them include laser ablation technique, carbon or electric arc discharge technique, chemical vapor deposition, pyrolysis, and electronic methods. Thess et al. (1996)reported that single-walled carbon nanotubes can be formed by condensation reaction of laser-vaporized C-Ni-Co (carbon-nickel-cobalt) mixture through laser ablation method. The process of condensation occurs at 1200 °C and the benefit of this technique is that it provides around 70% yield. Electron microscopy and XRD (X-ray diffraction) showed that they possess uniform diameter (0.2 Å) of single-walled nanotubes in ropelike structures having metallic properties. At 300 K temperature, their single-rope resistivity was observed to be $<10^{-4}$ Ω cm (Thess et al. 1996). In another method, carbon nanotubes were synthesized through arc discharge technique at very high temperature (more than 1700 °C) (Eatemadi et al. 2014). This high degree of temperature led to the expansion of carbon nanotubes with some structural defects as compared to the other processes. In this process, 6–10 nm highly pure water-cooled graphite electrodes were separated by a chamber containing helium in it at subatmospheric pressure (Grobert

2007; Eatemadi et al. 2014). The chamber contains some metal catalysts like iron, nickel, and/or cobalt, cathode and anode of graphites, and evaporated carbon molecules. However, yield of single-walled carbon nanotubes can be synthetically improved by adding either cobalt or transition elements like molybdenum, nickel, and iron with graphite (Iijima and Ichihashi 1993). Chamber was heated at 4000 K and pressurized by passing direct current through it (arcing process). This led to the evaporation and consequently solidification of half of the carbon on cathode tip, while the other remaining carbon accumulated on the periphery and condensed on the shoot of cathode. This will yield either multiwalled carbon nanotubes or single-walled carbon nanotubes (Eatemadi et al. 2014). Carbon nanotubes can also be prepared via chemical vapor deposition (CVD) and considered as one of the standard methods. It includes following types like HFCVD (hot filament chemical vapor deposition) (Ajayan et al. 1999; Dervishi et al. 2009), MPECVD (microwave plasma-enhanced chemical vapor deposition) (Ebbesen and Ajayan 1992), RF-CVD (radiofrequency chemical vapor deposition) (Bernholc et al. 1997), water-assisted CVD (Iijima et al. 1992; Journet et al. 1997; He et al. 2010), and CCVD (catalytic chemical vapor deposition) (Vander Wal et al. 2003). This process allows the expansion of carbon nanotubes and involves the breakdown of hydrocarbons. The process is somewhat similar to the arc discharge process. It also uses high temperature, i.e., 700 °C, with some metal catalyst particles like nickel, iron, and cobalt (Terrones-Maldonado 1997) or their combinations (Landi et al. 2005). First of all, the reactor was fueled with two different types of gases (the first one was process gas like ammonia, nitrogen, or hydrogen, while the second one was carbon-containing gas like ethanol, ethylene, methane, or acetylene) (Eatemadi et al. 2014). On catalyst, C-containing gas breaks down and carbon particles become visible. Hence, nanotube production takes place. However, this method is still under debate (Choudhary et al. 2014).

16.2.3 Classification of Carbon Nanotubes

Carbon nanotubes are generally made up of rolled sheets of cylindrical structures with aspect ratio of 108 (length to diameter) (Su and Cheng, 2014). On the basis of tube structure of carbon nanotubes, they are majorly classified into three groups: stacked-cup carbon nanotubes (SCCNTs), multiwalled nanotubes (MWCNTs), and single-walled nanotubes (SWCNTs) (Su and Cheng 2014). However, Jackson et al. (2013) classified carbon nanotubes in three categories: multiwalled carbon nanotubes, double-walled carbon nanotubes, and single-walled carbon nanotubes. Ganesh (2013) reported that carbon nanotubes can exist in two forms, either semiconductor or metals. Their function changes according to their structure and symmetry. Moreover, its diameter was observed to be 50,000 times thinner as compared to the hair of a human being (Ganesh 2013). In addition, they are considered to be stronger than steel also (Ganesh 2013). Structures of carbon nanotubes are so unique; they are hollow cylinders of graphite and possess hexagonally arranged carbon rings. Their end contains hexavalent arched structure while they are capped with pentavalent ring (Ganesh 2013) They possess high tensile strength which resembles with the property of graphene (Tománek et al. 2008). Tománek et al. (2008) also reported that they remain stable even at the extreme temperatures and maximize the vibrational entropy and configuration at low energy that led to the increase in temperature to hundreds of degree Celsius and thermal contraction in length (Tománek et al. 2008).

16.2.3.1 Single-Walled Carbon Nanotubes

The diameter of single-walled carbon nanotubes varies from 0.4 to 3 nm, while their length ranges in micrometer (Eatemadi et al. 2014). Aggregation of single-walled carbon nanotubes forms ropes or bundles. Single-walled carbon nanotubes are hexagonally arranged in a bundle and form crystal-like structures (Chico et al. 1996; Eatemadi et al. 2014). Single walled carbon nanotubes are classified into different forms according to type of wrapping, with chiral, zigzag, and armchair as evidences (Eatemadi et al. 2014). Properties of single-walled carbon nanotubes are same as compared to multiwalled carbon nanotubes except in high tensile strength (Vander Wal et al. 2003).

16.2.3.2 Multiwalled Carbon Nanotubes

The arrangement of multiwalled carbon nanotubes occurs in such a way that one carbon nanotube lies inside other carbon nanotubes. Moreover, the diameter of inner carbon nanotubes is generally less than the outer one. This type of model is known as Russian doll model, while in Parchment model, one carbon nanotube (graphene sheet) is surrounded or rolled by multiple copies of another carbon nanotube. It is thought that the function of outer wall is to protect the inner wall from chemical reactions (Eatemadi et al. 2014). Multiwalled carbon nanotubes contain many concentric hollow cylinders with interlayer spacing of 0.34–0.39 nm (Ajayan and Ebbesen 1997; Eatemadi et al. 2014). Diameter of inner wall decreases depending on the wall layers, i.e., the inner one varies from 0.4 mm to few nm, while the outer one ranges from 2 to 30 nm (Eatemadi et al. 2014). Ends of the multiwalled carbon nanotubes are closed with dome-shaped half fullerene capping.

16.3 Applications of Carbon Nanotubes

Human races are attracting toward the miniature objects which are facilitated by the use of nanoparticles. These nanoparticles are now used in even small things like chip (containing silicon nanoparticles) and to the large objects, for example, in large machines or robots. Similarly, the application of carbon nanotubes is increasing at an alarming rate which is described in the following section. Inventions in the area of nanotechnologies provide many new applications in the branch of aerospace, defense, electronics, and medical sciences (Liu et al. 2006; Wang et al. 2009b; Singh 2010; Khodakovskaya et al. 2013).

It is necessary to mention that the cumulative application of electronic devices with nanotubes gives an idea of its long-term applications (Endo et al. 2007). Conversely, carbon nanotubes show a scintillating class in the field of electronics like ballistic electronic conduction (Dekker 1999; Javey et al. 2003; Endo et al. 2007), solar cells (Huang et al. 2007), and fuel cells (Baughman et al. 2002). From year 2001 onward, progress in the field of carbon nanotubes was seen, after the invention of simple transistors to logic circuits. In addition, they are also frequently used in biological fields like imaging the live tissues and cells and detection of plaque by injecting carbon nanotubes after the microphages (Cherukuri et al. 2004). Images of photobleaching showed the affected area of plaque (Cherukuri et al. 2004). For measurement of blood count and for imaging of the tissue sections via fluorescence, single-walled carbon nanotubes were found to be useful (Cherukuri et al. 2006). Majorly the applications of carbon nanotubes are seen in the medical fields like tissue regeneration, biosensor analysis, and delivery of genes, drugs, and biomolecules (He et al. 2013). Generally, functionalized carbon nanotubes are used to fix on the surface of carbon nanotubes, which are then injected in animal cells either by targeting any specific cell or giving orally (He et al. 2013). The capsules of carbon nanotube drug are ingested by the cell, carbon nanotubes released all their contents and the drug is delivered (Liu et al. 2007; Zhang et al. 2010, 2011; Kateb et al. 2010; Singh et al. 2012; Usui et al. 2012; He et al. 2013). Functionalized carbon nanotubes are also capable to transport specific molecules across the nuclear and cytoplasmic membranes without showing any toxic effect (He et al. 2013). The drug conjugates proved very effective and safer than any other drugs (He et al. 2013). Carbon nanotubes are proved to be the promising material in context of its application in biotechnology (Wong et al. 1998; Azamian et al. 2002; Hong et al. 2010; Chen et al. 2015). They also act like transporter in animal cells (Liu et al. 2008), tumor cells (Kam et al. 2005), bacteria (Liu et al. 2009b), and plant cells (Khodakovskaya et al. 2011), which facilitates a new entry in the field of gene delivery (Chen et al. 2015). Moreover, they are also being used in agricultural fields to increase germination and promote root and shoot growth and biomass (Lin et al. 2009a, b; Liu et al. 2009a; Villagarcia et al. 2012; Khodakovskaya et al. 2013; Chen et al. 2015). In contrast, this is the era in which nanotechnology is still at its early stage in terms of development, even though they can significantly cause toxicity in plants, human health, as well as environment (Pidgeon et al. 2009). Stampoulis et al. (2009) and Khodakovskaya et al. (2011) reported that carbon nanotubes cause phytotoxicity by altering the expression of various genes. However for sampling of living biological cell, in vivo solid-phase microextraction techniques are also established (Ouyang et al. 2011; Lord et al. 2011; Chen et al. 2015). This technique is helpful because of its morphological structure, i.e., invasiveness in living organisms and smaller size, and provides the highly precise and more accurate data in very less time (Ouyang et al. 2011; Chen et al. 2015). Beside this, Lee et al. (2015) also demonstrated the application of carbon nanotubes in nanoelectronics, energy devices, and biosensors.

16.3.1 Uptake and Transportation of Carbon Nanotubes in Plants

There is a unique characteristic of plants that it contains cell wall which is a multilayered structure; that's why plant growth occurs in a fixed shape and possesses rigidity

(Serag et al. 2015). Cell wall of plants is surrounded by highly dense fibers of cellulose in which sugar polymers or glycans are embedded. This cell wall also acts as barrier for macromolecules, bacteria, and other parasites (McNeil et al. 1984; Serag et al. 2015). Crossing the barrier of cell wall of plants has now turned toward the beneficial impacts for various fields of biotechnology by applying genetic manipulation in it (Evans 1983; Serag et al. 2015). Pores of the cell wall are very narrow having a diameter of 5 nm that facilitates only the transport of selected macromolecules and allows to cross the barrier of solute materials (Meiners et al. 1991). Husen and Siddiqi (2014) also propounded that in water-suspended nanoparticles, plants either selectively absorb these nanoparticles or reject it. Carbon nanomaterials may be absorbed by the roots, but in seeds they create a hole for entry and then translocate in the shoots. After the entrance of carbon nanotubes in the plant organelles, they were shown to affect the growth and germination of plants (Khodakovskaya et al. 2012).

To overcome this problem, various enzymatic digestions were used to make it fragile so that it can be easily damaged by using any chemical and physical methods. However, there must be one precaution to look upon; osmolarity should be maintained for survival of cell or to prevent the cellular burst (Serag et al. 2015). There are several strategies that facilitate any substance or carbon nanotube to penetrate in the cell wall and plasma membranes. They are dependent on the ratio of size of carbon nanotubes to the pore size of the cell wall (Serag et al. 2015). The reported size of single-walled carbon nanotube is 1–2 nm, i.e., less than the pore size of the cell wall which is 5 nm. Thus, they are continuously leaked into the apoplastic region. Moreover, for shorter sized single-walled carbon nanotube, chemical methods like ultrasonic-assisted chemical oxidative cutting are used, and simultaneously carboxylic group is also used to introduce at the tip which increases their solubility in water (Nakayama-Ratchford et al. 2007; Serag et al. 2015). Now, the next barrier that occurs in the cell after removal of cell wall is the generation of protoplast. It was reported that the penetration of multiwalled carbon nanotubes occurs in the protoplast of *Catharanthus roseus* via nanoneedles (Pantarotto et al. 2004; Lacerda et al. 2012; Serag et al. 2015). The carbon nanotubes with large diameters have been reported to introduce in the cellulosic cell wall via hydrolysis. The cellulosic contents immobilized at the wall or tip of cup-stacked carbon nanotubes which resulted in local lesions from which carbon nanotubes could penetrate easily.

16.3.2 Cellular Uptake of Single-Walled Carbon Nanotubes

Serag et al. (2010, 2013) reported that due to the small size of single-walled carbon nanotubes, they were shown to easily penetrate in the cell wall pores of *Catharanthus roseus* and *Nicotiana tabacum*. In 2009, the first demonstration was shown about the uptake of single-walled carbon nanotubes in *Nicotiana tabacum* (Liu et al. 2009a). However, single-walled carbon nanotubes in *N. tabacum* showed temperature-dependent internalization through endocytosis. “Wortmannin” was reported as a second factor which inhibits the internalization or uptake of single-walled carbon nanotubes in plant cell. Wortmannin is a steroid metabolite that is extracted from the fungi named as *Penicillium funiculosum*, *Talaromyces wortmannii*, which prevents endocytosis-mediated internalization of single-walled carbon nanotubes (Serag et al. 2015). Serag et al. (2015) reported that *N. tabacum* cells used molecular cargoes as a cotransporter for transport of single-walled carbon nanotubes in different cellular compartments. Further, it is also reported that free form or conjugated form of fluorescein isothiocyanate (FITC) with single-stranded DNA was used for uptake of single-walled carbon nanotubes in the cells of *N. tabacum.* Moreover, Liu et al. (2009a) demonstrated that single-walled carbon nanotubes linked with free fluorescein isothiocyanate were internalized in vacuoles, while those FITC wrapped with single-stranded DNA were internalized in cytoplasm. Furthermore, it is evidenced that the free anionic form of fluorescein isothiocyanate after internalization in cytoplasm was translocated to vacuoles of cells through protein carriers (Oparka 1991). However, this process of translocation was seen to be inhibited by the probenecid (uricosuric drug) leading to the aggregation of fluorescein isothiocyanate in cytoplasm. The accumulation of FITC in the cytoplasmic region facilitates the entry of single-walled carbon nanotubes in the nucleus of *Catharanthus roseus* demonstrated by FRAP (fluorescence recovery after photobleaching) techniques, thereby inducing the autophagy in cells of *Catharanthus roseus* (Serag et al. 2015). With the help of raster scan image correlation spectroscopy (RICS), the location of SWCNTs was quantitatively determined in various compartments of *Catharanthus roseus* cells, and it was predicted that the diffusion coefficients of FITC linked with single-walled carbon nanotubes in vacuoles to cytoplasm were almost similar. This study revealed that autophagy leaks out the vacuolar cytoplasm. Autophagy is the process of self-eating of cells, which arises as a result of stress in the eukaryotic organisms and causes severe damage to different organelles of cells (Minibayeva et al. 2012; Serag et al. 2013, 2015).

The plants possess the property to reduce the phytotoxicity by inhibiting the accumulation of single-walled carbon nanotubes. Analysis through laser scanning confocal microscopy showed that plants distribute these nanotubes in different regions of vacuoles so that they expel it toward plasma membrane by vesicle-mediated transport pathway. Therefore, the vesicles containing single-walled carbon nanotubes were fused with plasma membrane and expelled outside the cell (Serag et al. 2010).

16.3.3 Cellular Uptake of Multiwalled Carbon Nanotubes

It is reported that in protoplast of *Catharanthus roseus*, multiwalled carbon nanotubes were physically penetrated via non-endosomal pathways. After injecting multiwalled carbon nanotubes via nanoneedles, images of TEM (transmission electron microscopy) showed its subcellular location in the membrane. Further studies from electron microscopy revealed that the internalization process via endosomal organelles is poorly linked with the multiwalled carbon nanotubes. However, this process is energy independent and proceeds via declining the rate of normal endocytosis process by inclining the concentration of multiwalled carbon nanotubes in the cell.

This process creates tonicity in the cell due to increased level of multiwalled carbon nanotubes in the cell medium. This led to the hindrance in the direct uptake of multiwalled carbon nanotubes in cells (Serag et al. 2010). However, direct internalization of multiwalled carbon nanotubes led to its translocation in various organelles such as nucleus, vacuoles, and plastids. These are the primary sites of multiwalled carbon nanotube accumulation. After its direct uptake, they start accumulating in perinuclear region of nucleus. Moreover, size-dependent localization of multiwalled carbon nanotubes occurs in cells of *Catharanthus roseus*; for instance, the multiwalled carbon nanotubes ranging from 30 to 100 nm were shown to be localized in vacuole, plastid, and nucleus region, while bigger than 100 nm tubes localized most of the organelles. Short multiwalled tubes (30–100 nm) resist to accumulate in the mitochondria and endoplasmic reticulum.

16.3.4 Beneficial Impact of Carbon Nanotubes in Plants

Development in the field of agricultural sectors is very necessary because most of the living beings depend on it. So, many researchers emphasized to work out in the field of nanotechnology-based enhancement of agricultural fields. They are trying to enhance the agricultural outputs, detection of diseases, and their remediation processes. In addition to this, they are also trying to increase the efficiency of plant to uptake more nutrients from soil (Table 16.1). This will ultimately lead to enhancement in overall increase of biomass and fruit of the plants (Fig. 16.2) (Serag et al. 2015).

Morla et al. (2011) reported to enhance the percentage of seed germination and seedling growth from multiwalled carbon nanotubes at 40 μg/ml concentration in *Lycopersicum esculentum.* Similarly, in *Medicago sativa* and *Triticum aestivum*, 10 nm multiwalled carbon nanotubes of 75% weight enhanced the seedling growth and elongated roots (Miralles et al. 2012). Moreover, Lahiani et al. (2013) observed enhanced rate of growth and germination in *Hordeum vulgare*, *Zea mays*, and *Glycine max*, from 25–100 μg/mL concentrations of multiwalled carbon nanotubes. Furthermore, in *Nicotiana tabacum*, 5 nm multiwalled carbon nanotubes at concentrations of 5–500 μg/mL led to the increased flowering and fruiting (Khodakovskaya et al. 2012). Beside this, Wang et al. (2012a) also observed increased cell growth and biomass from 50 to 630 nm O-MWCNTs in *Triticum aestivum.* Similarly, Tiwari et al. (2013) also demonstrated the effect of 6–9 nm multiwalled carbon nanotubes on *Lycopersicon esculentum.* They found that at a concentration of 40 μg/mL, absorption of nutrient elements was increased that ultimately led to enhanced growth and biomass of the plant. Tiwari et al. (2014) propounded the effect of 6–9 nm pristine multiwalled carbon nanotubes on transcription and morphology which includes enhanced uptake of water and essential nutrients leading to increase in biomass of the *Zea mays* plant. Likewise, in *Brassica juncea* and *Phaseolus mungo* plants, 20 μg/mL multiwalled carbon nanotubes increased the growth of roots (Ghodake et al. 2010). Furthermore, Mondal et al. (2011) also demonstrated the morphologically increased characters in *Brassica juncea.* They reported that 2.3×10^{-3} mg/mL concentration of 30 nm multiwalled carbon nanotubes in *Brassica juncea* showed enhanced length of roots (Table 16.1). However, Flores et al. (2014) found that single-walled carbon nanotubes also show beneficial effect on plant like *Rubus adenotrichos*. They found that at concentrations of 4 μg/ml, 1–2 nm, and 3.5–4 nm, carboxylic acid functionalized single-walled carbon nanotubes (SWCNTs-COOH); SWCNTs-Fe led to increased length of roots and shoots. In addition, improved cell metabolism was also observed. Furthermore, from 8–15 nm, SWCNTs enhanced rate of germination of plants *Lycopersicum esculentum* and *Allium cepa* (Haghighi and da Silva 2014). Additionally, Cañas et al. (2008) also observed that single-walled carbon nanotubes at concentrations of 9, 56, 315, and 1750 mg/L were shown to enhance the root elongation in *Allium cepa* and *Cucumis sativus*.

16.4 Inimical or No Significant Impact of Carbon Nanotubes in Plants

It is already discussed that the negative and positive impact of nanoparticles depends on several factors like size, concentration, ultrasonication, etc. (Ma et al. 2010). In the above section, at specific concentration(s) of carbon nanotube, some beneficial role in plants in terms of their morphology, physiology, or others was shown, while in this section, it is shown that some nanoparticles at different concentrations may cause phytotoxicity (Table 16.2).

For instance, Haghighi and da Silva (2014) demonstrated that 8–15 nm single-walled carbon nanotube at concentration of 10–40 mg/L in *Raphanus sativus* and *Brassica rapa* led to phytotoxicity by decreasing the rate of germination (Fig. 16.2). Tan et al. (2009) demonstrated that multiwalled carbon nanotubes at concentrations of 20 and 40 mg/L in *Oryza sativa* caused chromatin condensation, detachment of cell membrane from cell wall, and generation of reactive oxygen species and ultimately cause death of the cell (Table 16.2). Similarly, Begum and Fugetsu (2012) also reported that in *Amaranthus tricolor*, multiwalled carbon nanotube at concentrations of 500 and 1000 mg/L led to removal of red pigment from leaf, necrosis, curling, and wilting. In addition, they were shown to cause concentration-dependent reduction in root-shoot height, root-shoot weight, and leaf numbers which lastly causes death of the plant. It has also been demonstrated that in the plants of *Oryza sativa* and *Arabidopsis*, single-walled carbon nanotubes led to phytotoxicity by inducing cell aggregation, deposition of cell membrane, condensation of chromatins, and accumulation of H_2O_2 which ultimately causes death of the cell (Serag et al. 2015). Moreover, Shen et al. (2010) observed that 25% of death of cultured protoplasts occurs within 6 h after treatment with 25 mg/mL of single-walled carbon nanotubes. This occurs due to accumulation of ROS and finally led to the death (Shen et al. 2010; Serag et al. 2015). Similarly, hydroponic treatment of pristine multiwalled carbon nanotubes is observed to cause reduction in biomass of *Cucurbita pepo* (Serag et al. 2015). Lin and Xing (2007) and Begum et al. (2012) reported the phytotoxicity from carbon nanotubes in various plants. Begum et al. (2012) also demonstrated the reduction in root length and root fresh weight of

Cucumis sativus and *Oryza sativa* from multiwalled carbon nanotubes. It is also found that in *Cucumis sativus*, the length of roots declined in concentration-dependent manner. Furthermore, in *Hordeum vulgare* and ryegrass at 2000 mg/L multiwalled carbon nanotubes, the rate of germination decreased (Lin and Xing 2007). Chen et al. (2015) observed some black spots under light microscope and predicted its nanotoxicity by creating hindrance in transport of nutrients and also plant growth and development (Table 16.2). Cañas et al. (2008) reported the phytotoxicity of functionalized carbon nanotubes in lettuce at concentrations of 104, 315, and 1750 mg/L by decreasing the length of shoots, while functionalized single-walled carbon nanotubes at concentrations of 9, 56, 315, and 1750 mg/L showed no significant impact on phytotoxicity. Similarly, Yan et al. (2013) also observed no impact of single-walled carbon nanotubes at 20 mg/L concentrations in *Zea mays* seedlings. However, Stampoulis et al. (2009) reported that 13–16 nm multiwalled carbon nanotubes in *Zucchini* seedlings at concentration of 1000 mg/L showed reduced biomass but their seed germination remained unaffected.

16.5 Conclusion and Future Prospects

This review article discussed about carbon nanotubes, their major types and its applications in biological as well as nonbiological fields. Also, single-walled carbon nanotubes work differently from multiwalled carbon nanotubes. Although majorly positive functions of carbon nanotubes were reported in most of the studies, few carbon nanotubes at specific concentrations possess inimical or no significant impact on plant cell and their structures, because it is the characteristic of a nanoparticles that they may be toxic or beneficial depending on their concentration, size, shape, ultrasonication, etc. since each type of carbon nanotube (like oxidized multiwalled carbon nanotubes, functionalized single-walled carbon nanotubes, single-walled carbon nanotubes, multiwalled carbon nanotubes, water-soluble multiwalled carbon nanotubes, etc.) shows unique characteristic and properties and different functions on various plants at different concentrations and sizes. On seeing their highly advantageous role in plants, it can be predicted whether it can be supplemented to the plants as fertilizer or pesticide or expose their beneficial concentration on large scale in agriculture. Another method of utilizing it as a beneficial entity in agriculture is by using the biotechnological methods like gene delivery or manipulation because it is reported that carbon nanotubes can also pass from one generation to another (Tan et al. 2009). So, if they prove to be beneficial in first generation, they will exhibit positive role in second generation as well. It may enhance the quality and quantity of crops drastically, because many of the carbon nanotubes at specific concentrations change the morphology, the physiology, and even the genetic constitutions of the plant, ultimately, leading to increase in the biomass. So, it can be helpful in enhancing the biomass of agricultural fields at global scale.

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