

Nanotechnology in the Life Sciences

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Editors

Exploring the Realms of Nature for Nanosynthesis

 Springer

Nanotechnology in the Life Sciences

Series Editor

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Nano and biotechnology are two of the 21st century's most promising technologies. Nanotechnology is demarcated as the design, development, and application of materials and devices whose least functional make up is on a nanometer scale (1 to 100 nm). Meanwhile, biotechnology deals with metabolic and other physiological developments of biological subjects including microorganisms. These microbial processes have opened up new opportunities to explore novel applications, for example, the biosynthesis of metal nanomaterials, with the implication that these two technologies (i.e., thus nanobiotechnology) can play a vital role in developing and executing many valuable tools in the study of life. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale, to investigating whether we can directly control matters on/in the atomic scale level. This idea entails its application to diverse fields of science such as plant biology, organic chemistry, agriculture, the food industry, and more.

Nanobiotechnology offers a wide range of uses in medicine, agriculture, and the environment. Many diseases that do not have cures today may be cured by nanotechnology in the future. Use of nanotechnology in medical therapeutics needs adequate evaluation of its risk and safety factors. Scientists who are against the use of nanotechnology also agree that advancement in nanotechnology should continue because this field promises great benefits, but testing should be carried out to ensure its safety in people. It is possible that nanomedicine in the future will play a crucial role in the treatment of human and plant diseases, and also in the enhancement of normal human physiology and plant systems, respectively. If everything proceeds as expected, nanobiotechnology will, one day, become an inevitable part of our everyday life and will help save many lives.

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Preface

This book discusses the diversity in nature in all forms as far as the natural cohort-based nanomaterials synthesis protocols are concerned. Be it microbes, plants, wastes or any other allied source, the dictum stands tall—nanoscale remains the scale of nature! Nowadays, bionanotechnology is considered as one of the most exciting and upcoming branches of nanotechnology where possibilities seem endless. Actually, physics, chemistry and biology have equipped us with the knowledge of molecular structure, properties and functions which have to be smartly engineered at nano-level to realise various technological applications. Chapter 1 details and emphasises this very fact by delineating different examples and possibly involved thermodynamic mechanisms. Microbes, the minuscule nano-assemblies of nature, have been explored for the purpose of synthesis as they best communicate and deliver as per their cellular level organisation which is very well presented in Chaps. 2 and 3. Chapters 4–9 emphasise the potential promises of different phyto cohorts and their uses in the immediate future. Chapter 10 delineates the use of biogenic silver and gold towards mitigation of dye-related pollution in our aquatic ecosystems. An epoch approach towards waste utilisation has been suggested in Chap. 11 which is bound to have a long-term impact in terms of our knowledge. Chapters 12–14 describe the inherent protocols being utilised by the morphons, broadly unknown to us. While graphene-based biomedical applications have been suggested in Chap. 15, two other chapters (Chaps. 16 and 17) detail the diagnostic prodigality of nanomaterials towards protection of crop plants from microbial annihilation and crystallisation of cellulose nanoparticles, respectively.

This comprehensive book covers the realm of nature and should enlighten readers everywhere.

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Ram Prasad
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Kamal Prasad

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Chapter 1

Mechanistic Plethora of Biogenetic Nanosynthesis: An Evaluation



Anal K. Jha and Kamal Prasad

“You got to accept Nature the way she is not the way you want her to be.....”

Richard Feynman.

1.1 Introduction

The Mother Nature seems a superlative manifestation of nano-sized assemblies at its different level of organizations and in general obeying the principles of supramolecular chemistry and thermodynamics. Right from the primitive prokaryotes to the advanced and better organized eukaryotes, inorganic materials have proved their prodigality with time. Nature commenced its organizational endeavor taking use of inorganic materials for various purposes and this indeed led to the development of a myriad of organic structures and subsequently the living systems. This speaks at large of it regarding the time survived interaction of inorganic materials and biological systems. Stress has been a testing cue for the exponential process of evolution which provided various organisms to evaluate and subsequently modulate their metabolic weaponry in order to ensure their survival on this planet. These weapons of adaptability have helped the humanity by all possible means. Right from nutrition to therapeutics, primary or secondary metabolites have proved their utility.

Over the last few years, the scientific and engineering communities have been witnessing an impressive progress in the field of nanoscience and nanotechnology. It is observed that the reduction of materials' dimension has pronounced effects on

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the physical properties that may be significantly different from the corresponding bulk material. Various physical properties which different nanomaterials are being exhibited are due to: large surface atom, large surface energy, spatial confinement, reduced imperfections, etc. One key aspect of nanotechnology concerns the development of rapid and reliable experimental protocols for the synthesis of nanomaterials over a range of chemical compositions, sizes, high monodispersity, and large-scale production because the synthetic protocols and their processing parameters have large effects on the ultimate properties or performances. Accordingly, many synthetic procedures have emerged with time for the preparation of inorganic nanomaterials most of them capital, time, labor and/or more alarmingly the environmental concerns. Eyebrows were raised genuinely with respect to such protocols as they could not shrug off the fate of the participating chemicals in our immediate milieu. Promulgated laws and framed legislations like WEEE and RoHS restrict the use of such protocol which threatens our survival on this planet. Therefore, synthesis of plethora of nanomaterials ranging from metals and alloys to oxides and chalcogenides, etc. using green protocols is of the major concern nowadays. The objective of this chapter is to address the possible involved synthetic mechanisms in different nanotransformations.

1.2 Synthesis Accomplished by Soft Chemicals

Natural cohorts are very rich in metabolites of a primary or secondary type, and primary ones often take lead in the procedure of nanotransformation for being comparatively labile and regenerative. Organic acids are proven and time tested chelators and often do act as redox agents broadly banking upon the working environment. They indeed act as soft chemicals and help in synthesis of nanomaterials. In order to exemplify, ceramic perovskite with ABO_3 type structure is considered here, which are technologically very important and find applications in multilayer capacitors, ferroelectric, piezoelectric, pyroelectric, memories, solid oxide fuel cells, energy harvesting, microwave, etc. When considered a cubic structure, the oxygen atoms form a cubic lattice of corner-sharing octahedra with B-cations at their centers while A-cations form a second interpenetrating cubic sub-lattice located at 12-fold coordinated sites between the octahedra. The different principles of chemistry which can be combined (viz. ionic radii, valence state, tolerance factor, etc.) to obtain numerous complex perovskite oxides with the mixed-cation formula such as $(A'A''...)BO_3$, $A(B'B''...)O_3$, or $(A'A''...)(B'B''...)O_3$ have a variety of interesting properties, designed for many electronic and/or microelectronic devices (Rödel et al. 2009; Damjanovic et al. 2010; Prasad et al. 2014). Additionally, it has been observed that modifications either at A- or B-site play an important role in tailoring different properties of complex perovskites as the material's properties largely depend upon the size difference of pseudo-cation $(A'A''...)^{2+}$ and/or $(B'B''...)^{4+}$ and on the difference on their valence states. With the intension to realize the optimal properties of such complex perovskite oxides, synthesis of single-phase compound

is the foremost requirement. It is known that the processing technique and/or conditions play very important role in deciding the material's properties. Accordingly, the synthetic mechanisms of ABO_3 using two soft chemical techniques namely citrate gel and tartrate gel methods are being considered here keeping in view of the fact that these organic acids are found in many plants and fruits too.

Organic acids ($R-COOH$) often make a non-equivalent resonating structure, whereas $RCOO^-$ efficiently makes an equivalent one. In this arrangement, the resonance energy of stabilization of $R-COOH$ goes higher than that of $RCOO^-$ and this energy of dissociation probably remains available all along in the incubation medium for nanotransformation of both metal and oxide system, as the case may be (Morrison and Boyd 1983; Jha et al. 2011; Kumar et al. 2013). In case of citrate gel method, citric acid and citrate ions are considered readily inter-convertible requiring and/or releasing an appreciable amount of free energy (~ 47 kJ/mol) in aqueous medium, which is probably sufficient to accomplish nanotransformation (Fig. 1.1). This may be a very common case with citric acid but with higher one like tartaric acid the case may be often much amenable. It is found that tartaric acid (H_2Tart) is energetically astir molecule, aptly displaying an interesting pattern of optical isomerism. The mean value for heat of combustion for tartaric acid was calculated to be 1124.5 kJ/mol recently (Kochergina et al. 2006). The value of heat of dissociation was estimated to be of 27.17 kJ/mol for the temperature above $50^\circ C$ (Bates and Canham 1951). It clearly indicates that this energy is in all probabilities sufficient to accomplish a nanotransformation (Fig. 1.2). Further, this procedure involves com-

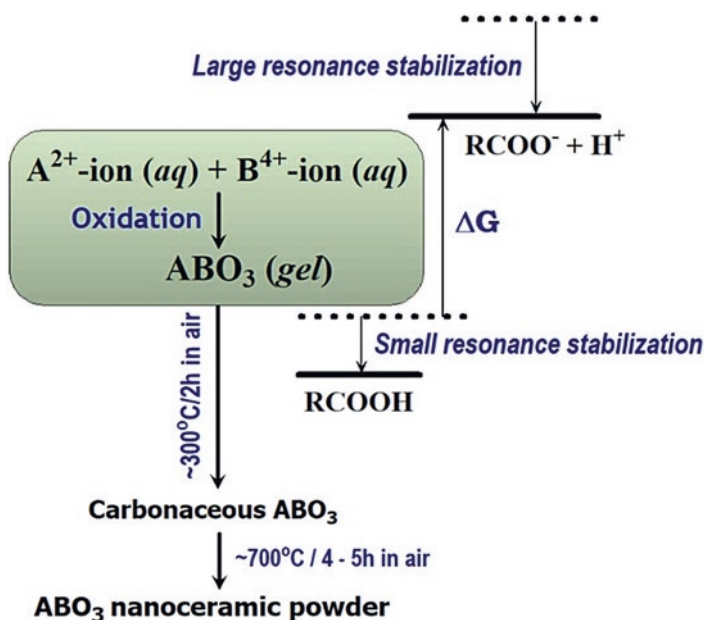


Fig. 1.1 Schematic for the synthesis of nanocrystalline ABO_3 powder using citric acid gel method

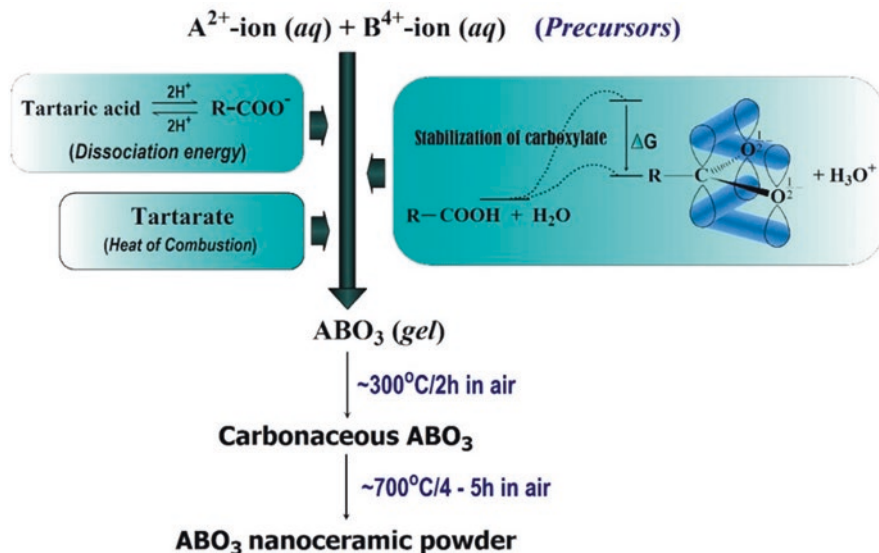


Fig. 1.2 Schematic for the synthesis of nanocrystalline ABO_3 powder using tartaric acid gel method

plexation of metal ions (A^{2+} and B^{4+} in this case) by polyfunctional carboxylic acids, such as tartaric acid having one hydroxyl group. Upon heating the mixture, the solvent (water) parches culminating into heightened viscosity. After complete parching of water, the mixture turns into a gel form and its constituents are mingled at atomic level. The gel upon heating at higher temperature ($\sim 700^\circ\text{C}$, 4–5 h) produces the nanomaterial of our choice (e.g., nanoceramic like (ABO_3)) which might be due to the combustion of organics present in the gel, along with the evolution of gases during calcination (Kumar et al. 2015). In the present soft-chemical methods, the interactions of citric or tartaric acid with A^{2+} and B^{4+} ions in stoichiometric ratio could make it possible to lower down the surface energy. Therefore, the effect of such soft-chemical ambience could have made the reaction to occur more easily. Higher congeners may also be employed for this purpose depending upon the material to be synthesized.

1.3 Biosynthesis of Inorganic Nanoparticles

Bionanotechnology, an upcoming and exponentially promising branch of Nanoscience & Technology, refers to the materials and processes at nanometer scale that are based on biological, biomimetic, or biologically inspired molecules. The procedures of preparation of nanoparticles from different biological sources using bionanotechnology approaches could be highly diverse and broadly dependent upon

the individual source being employed and its cellular constitution which are discussed in detail in different chapters of this book.

1.4 Biosynthetic Mechanisms

The process tangled in the synthetic cues of nanoparticles, whether metals or oxide, seemingly appears heaped in the responsive culmination of the biological system, congener morph on being taken into use and its immediate metabolite ambiance along with basic bustles of metabolism or its total biochemical and/or metabolite content.

1.5 Microbial Systems

1.5.1 Prokaryotes

As per their nomenclature, prokaryotic systems have obliterated nuclear assembly and cluttered cytoplasmic organization. Metabolite content is also poor in every respect compared to their other advanced congeners (eukaryotes) yet they face challenges of nature in most adroit manner by all viable means. Under metallic stress, their first line response originates from the membrane itself in the mode of a negative electro-kinetic potential, that helps to attract metal ions, and this step subsequently acts as pivot for initiation of nanomaterials synthesis. Further addition of a regular nourishment carbon source such as glucose which works as a soft reducing agent tends to lower the redox potential. The oxidation-reduction potential is asserted to be quantitative character as a degree of aerobiosis and is denoted by rH_2 . This can be perceived as a negative logarithm of gaseous hydrogen as its partial pressure. Let us consider the representative example of *Lactobacilli*, they are Gram-positive akin to generate lactic acid through homo and/or hetero-fermentative carbohydrate metabolism. They constantly tend to retort to undulating environmental conditions, which affect their physiological state and consequently their growth rate. Periods of slow growth and non-growing states are often followed by short intervals of fast growth. Mostly, cells of the bacteria remain in a slow or sluggish state to escape cell mortality and lysis under limitation of nutrients (C, N, P, metal ions) and other energy source (Gallegos et al. 1997; Hantke 2001). The *Lactobacilli* are physiologically compelled to constantly regulate the cytoplasmic or intracellular pH. The cells incapable of maintaining the same tend to lose function and viability. Recently, an approach to understanding the pH regulation in cytoplasm has emerged despite pH homeostasis in *lactobacilli* being very important (Hutkins and Nannen 1993).

The principal metabolic product lactic acid is one of the smallest molecules with an asymmetrical carbon in the location of the carboxylic function. This unique feature allows its existence with two defined stereo-isometric forms called L(+) and D(-). In addition to its optical activity, its coetaneous carboxylic and hydroxyl groups concede it to react either as an acid or as an alcohol. This dual functional approach initiates the spontaneous formation on intermolecular esters (oligomers) with a discharge of water, which leads to a thermodynamic equilibrium dependent on the solution concentration and age. The pace of this reaction of condensation is aligned to the temperature and the possible presence of catalyst species (Lewis acid), and to the equilibrium gap of the solution under consideration. As for every esterification reaction, it is reversible by adding water (hydrolysis of formed oligomers). Thermodynamically, heat of dissociation (ΔH amounts to 63 cal/mol (at 25 °C), and the equivalent of free energy of dissociation (ΔF amounts to 5000 cal/mol for lactic acid (www.lactic.com/index.php/lacticacid 2009)). This probably ensures ready availability of energy in the culture medium, which along with other crux metabolic fluxes, leads to a successful nanotransformation. Earlier works on molecular level have successfully deciphered the innards of stress response in *Lactobacilli*. Dual integral systems, or histidine-asparagine phosphorylase (HAP) schemes, denote machinery for signal transduction that is extensively suffused among bacteria. Generally, however, these systems have two components: a histidine protein kinase (Hpk) with a response regulator (RR). The Hpk has an N terminal extracellular sensor domain, while the C-terminal portion is made up of protein remains in the cytoplasm. The RR is cytoplasmatic and bears a receiver domain and binds to the DNA component (Robinson et al. 2000). The Hpk acts as a sensor and is extracellular. Once a sudden alteration is found in the ambience, it signals in the form of phosphorylation, via a conserved histidine in the Hpk, to an asparagine residue in receiver segments of the RR (Robinson et al. 2000). Immediately upon phosphorylation, the RR is activated and the DNA-adhering region adheres to the DNA, as a transcriptional enhancer or repressor, hence changing the gene assertion of the cell. As such, 16 two elemental signal transduction could be tangled for regulating the phenomena such as genetic competence (Tortosa and Dubnau 1999), an adaptation to various stresses (Mizuno and Mizushima 1990; Morel-Deville et al. 1998), etc. *Lactobacilli* in general lack a two-component system. *L. acidophilus* encodes nine systems (Altermann et al. 2005) and *L. plantarum* 13 (Kleerebezem 2004).

Under many situations, the transduction of a signal is often more complex than described above. Deciphering gene regulation will increase our knowledge as to how this organism acclimates and interacts in its habitat or against metallic stress. Cells of a probiotic microorganism like *L. sporogenes* are well equipped for undertaking any shear created by toxins or metal ions. This could be accomplished at defined echelons beginning from molecular (genomic/transcriptomic and proteomic levels) through the much trusted metabolomic level to the cytoplasmic one (Urban and Kuthan 2004). Plasmids are commonly found in many members of the *lactobacilli* at the molecular level (Gasson and Shearman 2003). Most of these plasmids are cryptic (Shareck et al. 2004), but their bestowal and significance to the harboring strain remains obscure or unclear. Meanwhile, in *L. plantarum* WCFS1, three

plasmids have been functionally deciphered. Two among them had no other function except replication, while the largest plasmid pWCFS103 (36 kb) negotiating resistance to arsenate/arsenite was found to be conjugative (van Kranenburg et al. 2005). The metabolic detoxification takes place using glutathione and thioredoxin (Penninckx 2000; Sundquist and Fahey 1989; Holmgren 1985) and the oxidizing environment ensures biosynthesis of nanoscale oxides or chalcogenides. Further, in the cytoplasm the metal ions may undergo complexation once a suitable candidate ligand is available or finally through the vacuolar retention (Serrano 2008).

1.5.2 Eukaryotes

The ambience of living cohorts exponentially tends to fluctuate; therefore, resilience to the shears of the environment is necessary for organisms to persist. Chemical-stress-inducing factors like pollutants (organic or inorganic) might have different pattern of action but the annihilation stands the same. Along with this, certain natural shearing factors like radiation are also assorted with oxidative damage in cells (Avery 2001; Limon-Pacheco and Gonsebatt 2009). Encountered by metal/metalloid toxicity, fungal members switch on response at manifold levels emanating from cell wall to nuclei that can be understood as follows:

- (a) Production of nanoparticles using filamentous fungi has some influence over other organisms. Filamentous fungi are handy, want simple raw materials, and have raised wall-binding capacity (Ray et al. 2011). Members of fungi also harbor a good number of hydroxyl/methoxy derivatives of quinones such as benzoquinones and toluquinones, which are secreted especially by the members of the lower fungi (for example, in *Penicillium* and *Aspergillus* species) in retort to a potential metallic stress. Presence of these metabolites often starts a redox reaction due to tautomerization that leads to synthesis of a nanomaterial (Jha et al. 2009a). Cell membranes are commonly entrusted with like peptides and proteins having small molecular mass and those are cardinally important elements of almost all metal/metalloid detoxification processes, and hence the caliber of extracellular and cytosolic chelation reactions cannot be disparaged (Tamás and Martinoia 2005; Azcón-Aguilar et al. 2009; Wysocki and Tamás 2010; Prasad et al. 2016).

The oxidoreductases, which are either membrane based or cytosolic, could have an indispensable role in the procedure. The pH sensitive oxidoreductases always tend to work in an alternative manner. A lower pH triggers oxidases while a higher value tends to activate the reductase (Jha et al. 2009a). Amino acids and amino acid-derived molecules have a high significance in plants to adapt in heavy metal assault conditions. Nitrogen-containing primary metabolite mainly proline is frequently observed to be incorporated once a heavy metal assault caused by cd, cu, Ni, or Zn is encountered. Proline is bestowed with three main functions in metal detoxification such as binding with metals,

signalling, and antioxidative defense (Shanti and Karl 2006). Elaboration of inorganic metal chelators illustriously documented along numerable members of fungi and especially among brown-rot and white rot fungi and this process seems to be stimulated under Cu(II) and Cd(II) stress (Clausen and Green 2003; Jarosz-Wilkolazka and Gadd 2003). The substantive formation of water-insoluble metal-oxalate crystals is unequivocally an apt way to circumvent toxic metal ions, which tend to enter fungal cells (Jarosz-Wilkolazka and Gadd 2003). In addition to this, oxalate is important to preserve lignolytic system of white rot basidiomycetes (Clausen and Green 2003). A vast range of fungi has been established to produce extracellular mucilaginous materials (ECMM or emulsifier) with excellent toxic metal binding capabilities (Paraszkiewicz et al. 2007; Paraszkiewicz et al. 2010; Paraszkiewicz and Długóński 2009). The production of various metabolites like citric acid, homogeneous proteins, heterogeneous proteins, and peroxidases by fungi make them quite effective for detoxification of heavy metals from industry-based effluents. White rot fungi are very widely spread among genera and their enzyme-producing activity makes them effective decolorizers to eliminate toxic metals by biosorption ultimately comprehending the effluents more eco-amenable (Tripathi et al. 2007). The level of oxalic acid is significantly high in comparison to other acids like malonic acid, citric acid, shikimic acid, lactic acid, acetic acid, propionic acid, fumaric acid, formic acid, iso-butyric acid, and butyric acid among different acids production that are present in variable concentrations (Ulla et al. 2000). In addition, *Fusarium Oxysporum*, *Aspergillus niger*, *Aspergillus fumigatus*, and *Penicillium brevicompactum* being eukaryotes have been bestowed with a much better organized cellular system compared to the bacteria. Therefore, a drastic reduction in particle size of nanomaterials, which is being reported, is natural. *Fusarium* and other members are a benefit to the kingdom fungi. Their adaptability is prodigal, which is manifested as metabolic treasures from membrane-bound cellulases, nitrate reductases, galactosides, and quinones to cytosolic oxidoreductases like cytochrome P450 (Durán et al. 2005), and an active FAD-containing form of nitroalkane oxidase is also present (Gadda and Fitzpatrick 1998).

- (b) Cells of eukaryotes, after encountering a metallic stress, may trigger their metabolomic machinery and that can be displayed as intracellular chelation and compartmentalization. Among the usual assaults could be fluctuating osmolarity, swinging level of nutrients, availability of virulent molecules, and inclement temperature. While multi-cellular, locomotory morphons can share such assaults but their uni-cellular congeners like yeast are submitted to the clemency of their milieu and either have to respond or cease (Morano et al. 2012).

Metal ions enter the cells through multiple transporters and tend to annihilate the normal course of metabolism and compel the cell to trigger its stress shearing mechanisms and because of such cues, nanomaterials are synthesized. However, the deliberate elimination of the few plasma membrane channels and transporters is noted to confer metal tolerance to metal/metalloid exposed *S. cerevisiae* cells (Tamás and Martinoia 2005; Wysocki and Tamás 2010).

Though, the cells also harbor other chelation sources such as GSH complexes and phytochelatin complexes for the different ionic species such as Cd(II) , As(III) , Hg(II) , and Pb(II) . The actual mechanism could be intricate as it comprises multiple molecular level transporters and seems something beyond the scope of this chapter.

However, the main metabolite contributing towards detoxification procedures among cells of yeast is reckoned to be glutathione (GSH) along with two other groups of metal adhering ligands like metallothioneins and phytochelatin, both very well deciphered. Bearing a structure of c-Glu-Cys-Gly , a tripeptide, they are aptly tangled with enumerable metabolic bustles among bacteria, yeasts, plants, and animals. The *sui generis* properties of an excellent nucleophile places this molecule as a potential detoxifier undertaking bio-reduction with utmost agility and thereby rendering defense against annihilation of free radicals and xenobiotics. GSH also makes a structural unit in molecules of phytochelatin that is one of its major activities. Copied from mRNA translation, metallothioneins are low molecular weight metal binding proteins, very rich in cysteine (Kagi and Schaffer 1988). A considerable number of cysteine fragments bind different metals by S–S bonds. Metallothioneins are classified according to the arrangement of these residues (Butt and Ecker 1987). Bearing a specific sequence of defined amino acids like cysteine along with a low content of other aromatic amino acids, the acumen to adhere metal ions is quite common with metallothioneins (Mehra and Winge 1991). A dedicated clan of genes encodes such a significant protein. Albeit, a model for Cu^{2+} ions detoxification has been created but it suffices other metals in yeast (Mehra et al. 1988). The assault of Cu^{2+} and Zn^{2+} is assorted cadmium toxicity among animals and there are evidences that this significant natural chelator may play similar role among a few plants and yeast (in *S. cerevisiae* and *C. glabrata*) (Murasugi et al. 1983; Grill et al. 1985).

First discovered in the yeast *Schizosaccharomyces pombe* (Cobbett 2000), but found to quite common among most of the plants (Cobbett 2000; Rauser 1995) and a few animal cohorts (Kondo et al. 1983). Initially, though principally described as cadmium-binding peptides (Cobbett 2000; Rauser 1995), synthesis of phytochelatin is triggered by large number of metal ions such as Cd^{2+} , Pb^{2+} , Zn^{2+} , Sb^{3+} , Ag^{+} , Ni^{2+} , Hg^{2+} , HAsO_2^- , Cu^{2+} , Sn^{2+} , SeO_2^- , Au^{+} , Bi^{3+} , Te^{4+} , and W^{6+} , whenever supplemented to the medium (Huang et al. 2007). Phytochelatin bearing a common arrangement (c-Glu-Cys) $_n$ -Gly, where $n = 2-11$, with a multitude of structural variants that have been detailed in the literature (Grill et al. 1989; Rauser 1995; Zenk 1996) also make a promising detoxification system among plants. They are structurally akin to the GSH, performing the function of their substrate during their enzyme biosynthesis, the fact that has broadly been authenticated by physiological, biochemical, and genetic persuasions (Grill et al. 1989; Rauser 1995; Zenk 1996). The synthesis of phytochelatin commences within very small span of time once yeast cells are bared to cadmium ions and is regulated by enzyme action in the company of metal ions. Among the best-reckoned activators are cadmium ions, followed by

ag, Bi, Pb, Zn, Cu, Hg, and au (Clemens et al. 1999; Ha et al. 1999; Vatamaniuk et al. 1999). In plants and yeast, Cd-phytochelatin complexes are fabricated in the cytosol but are ameliorated in vacuoles (Salt and Wagner 1993). Specific studies of the fission yeast *S. pombe* deciphered that nearly the whole cadmium and phytochelatin amounts are localized in vacuoles (Mehra and Mulchandani 1995). In comparison to metallothioneins, phytochelatins harbor many appreciable advantages attributable to their structure and specifically the repeated *c*-Glu-Cys units and hence have a better metal binding capacity (Mehra and Mulchandani 1995). Further, phytochelatins can accommodate high quantity of inorganic sulfur culminating into an increased capacity of binding to cadmium (Mehra et al. 1994). The procedure of bio-mineralization of cadmium by the yeast congeners *S. pombe* and *C. glabrata* is a metal-induced biotransformation, in which metal ions are there upon chelated with small choosy peptides and coprecipitated with inorganic sulfur, resulting in nontoxic monodisperse CdS clusters with an average diameter of 2 nm. The crystal lattice consists of 85 CdS pairs covered by approximately 30 (*c*-Glu-Cys)*n*-Gly peptides, with $n = 3-5$ (Dameron and Winge 1990). Vacuoles are the primary sites of intracellular metal/metalloid sequestration and storage in fungi (Tamás and Martinoia 2005; Wysocki and Tamás 2010).

- (c) As and when exposed to toxic metal/metalloid annihilation, fungal cells face oxidative cell injuries (Avery 2001). Fungi have well-prepared weaponry of antioxidants to circumvent different kinds of such stresses. GSH-independent and GSH-dependent enzyme activities are capable of overcoming reactive oxygen species with remarkable efficiency (Perego and Howell 1997). While elevated temperature represents the primary assault like heat shock (as described above), among major secondary consequences is production of reactive oxygen species (ROS). All organisms are vulnerable to ROS during the process of normal aerobic metabolism or punctuated by a disclosure to radical-forming compounds (Lewinska and Bartosz 2007). Normally, the molecular oxygen is relatively non-reactive and benign but under partial reduction, they may produce a number of ROS that includes superoxide anion and hydrogen peroxide ($H_2O_2^-$) and can further react to produce the highly sharp hydroxyl radical. Reactive oxygen species (ROS) are toxic to the cellular components culminating into lipid peroxidation, protein oxidation, and DNA modification (genetic damage). *S. cerevisiae* React to an oxidative shear using a number of cellular reactions, which ensure the existence of the cell following disclosure to potentially threatening oxidants including defense systems that detoxify ROS, reduce their rate of production, and repair the damage being created by them. Many responses are ROS-specific, but there are also general stress responses that are typically invoked as a reflex to diverse stress conditions (Bun-Ya et al. 1992). Among metabolically labile morphons, ROS are constantly generated and in *S. cerevisiae* the mechanism to shear such assaults is very well developed in order to maintain a reducing intracellular environment. An oxidative shear is generally understood to have taken place when ROS overcome these countering pro-

cedures, resulting in genetic degeneration and physiological impairments, leading eventually to cell mortality. Antioxidant defenses encompass an integer of protective enzymes that are found in different subcellular compartments and may be upregulated in response to ROS exposure. Nonenzymatic defenses typically consist of small molecules that can actually function as free radical scavengers; to date, only ascorbic acid and GSH have been extensively characterized in yeast (Bun-Ya et al. 1992). Antioxidants, like vitamin C, can reduce transition metals giving these compounds a pro-oxidant character (Hiltunen et al. 2003). The different conglomerate of enzymes convoluted in the process of conservation against ROS exposures among fungi may briefly be introduced as follows:

Catalases. Catalases are ubiquitous heme-containing enzymes that catalyze the disalteration of H_2O_2 into H_2O and O_2 . Yeast has two parallel enzymes: The peroxisomal catalase A encoded by CTA1, and the cytosolic catalase T encoded by CTT1 (Hiltunen et al. 2003).

Superoxide dismutases. Superoxide dismutases (SODs) convert the superoxide anion to hydrogen peroxide, which can eventually be reduced to water by catalases or peroxidases (Hiltunen et al. 2003). SODs are pervasive antioxidants, which vary in their intracellular locale and metal cofactor urgencies among different organisms (Dean et al. 1997).

Methionine sulfoxide reductase. Amino acids are vulnerable to oxidation by ROS (Le et al. 2009). Most organisms contain methionine sulfoxide reductases (MSRs), which protect against oxidation of methionine through catalysis of thiol depending on the reduction of the oxidized residues of met.

Thioredoxins. *S. cerevisiae*, Like most eukaryotic morphons, has a cytoplasmic thioredoxin system, which operates in rendering protection against oxidative stress. This comprises two thioredoxins (TRX1 and TRX2) and a thioredoxin reductase (TRR1) (Gan 1991). As in most cohorts, yeast thioredoxins are agile as antioxidants and are critical in protecting against oxidative stress induced by various ROS (Kuge and Jones 1994; Pedrajas et al. 1999).

Peroxiredoxins. Peroxiredoxins (Prx) have multiple roles in stress protection, acting as antioxidants, molecular chaperones, and in the regulation of signal transduction (Pedrajas et al. 1999).

The glutathione system. The oxidation of sulfhydryl groups is one of the earliest detectable advent during ROS conciliated damage. This directionalizes the signification of GSH (g-glutamylcysteinylglycine), which is typically found as the most copious low molecular weight sulfhydryl compound (mM concentrations) in most organisms. Many roles have been advised for GSH in a miscellany of cellular procedures including amino acid transport; synthesis of nucleic acids and proteins; inflection of enzyme activity; and metabolism of carcinogens, xenobiotics, and ROS (Grant et al. 1996a). Not uncommonly, therefore, GSH is an indispensable metabolite in eukaryotes, and for example, mice that are trailing in GSH biosynthesis expire rapidly (Vina 1990). Similarly, GSH is an indispensable metabolite in yeast where

it is seemingly essential as a reductant during natural growth conditions (Grant et al. 1996b).

Glutaredoxins. Glutaredoxins (GrX) are heat stable and small oxido-reductase reported firstly from the *E. coli* in which they were found to be a potential hydrogen donor to ribonucleotide reductase (Holmgren 1989).

Glutathione peroxidases. Eukaryotic glutathione peroxidases are the main defense against oxidative assault caused by hydroperoxides. They reduce hydrogen peroxide and other organic hydroperoxides, like fatty acid hydroperoxides, to the analogous alcohol, using their reducing power provided by GSH (Inoue et al. 1999).

- *Glutathione transferases*. Glutathione transferases (GSTs) are the main family of proteins, which are muddled in the curing of many xenobiotic compounds (Sheehan et al. 2001). They catalyze the conjugation of electrophilic substrates to GSH prior to their removal from cells via glutathione conjugate pumps. Two genes encoding functional GSTs, cognominated GTT1 and GTT2 have been identified in yeast (Choi et al. 1998).
- *Ascorbic acid*. Ascorbic acid is a water-soluble antioxidant, which commonly acts in a redox couple with glutathione in many eukaryotes (Winkler et al. 1994). However, the relevance of ascorbate to the yeast oxidative stress reply is obscure since yeast contains a 5-carbon analog, erythroascorbate that can have limited importance as an antioxidant. Using these facts the detailed discussions on the synthesis of different metals, oxides, or chalcogenides using microbes have been undertaken (Jha et al. 2007, 2008, 2009b; Jha and Prasad 2010a, b, c, 2014a; Prasad and Jha 2009; Prasad et al. 2007, 2010).

1.6 Plant Systems and Food Beneficiaries

The deluge of plant-mediated transformation potential is quite vast or seemingly exponential. Seemingly, each member of the plant kingdom in nature is ready to negotiate a nanotransformation as either a metal or an oxide depending upon its own metabolic treasure—the sole factor obligated for survival against the gamut of environmental rigors. Recently, enumerable research has been presented regarding plant-assisted biosynthesis of metallic nanoparticles and the chargeable phytochemical candidates have broadly been identified to be flavones, ketones, aldehydes, amides terpenoids (citronellol and geraniol), and carboxylic acid in the vigil of detailed IR studies. A quick reduction of Ag ions during a few recent investigations might have culminated due to involvement of water-soluble phytochemicals like flavones, quinones, soluble sugars, and organic acids (such as oxalic, malic, tartaric, protocatechuic) abundantly found in plant tissues (Prasad 2014). Phyllanthin and hypophyllanthin (lignan) adjudicated synthesis of Ag and gold (Au) nanoparticles

has been noted recently (Kasthuri et al. 2009). Using *Eclipta* leaf extract, Ag nanoparticles were synthesized and a candidate phytochemical was accounted to be flavonoids (Jha et al. 2009c). *Cycas* leaves have been found to contain amentoflavone and hinokiflavone as characteristic biflavonyls, which have been found to synthesize Ag nanoparticles (Jha and Prasad 2010d). Synthesis of Au nanoparticles negotiated by Bael (*Aegle marmelos*) leaves has been noted recently (Rao and Savithamma 2011; Jha and Prasad 2011). Higher plants belonging to the xerophyte, mesophyte, and hydrophyte categories were recently assayed for their nanotransformation promises and all were found suitable for biosynthesis, meeting their inherent metabolic obligations (Jha et al. 2011). Earlier, by using *Aloe vera* (Sathishkumar et al. 2010), Neem (*Azadirachta indica*) (Chandran et al. 2006), *Emblica* (Ghule et al. 2006), and *Avena* (Narayanan and Sakthivel 2008) leaf broth metallic Ag was synthesized. A split-second biosynthesis of Ag nanoparticles in the above reported investigations is net culmination of reductive properties of water-soluble phytochemicals such as flavones, quinines, and organic acids that are generously present in the parenchymatous tissue of leaves (Chandran et al. 2006). Synthesis of nanoscale Ag was reported using mature chili fruit (*Capsicum annum L.*) (Ghule et al. 2006) and orange juice (Jha et al. 2011). Here the synthesis of nanoscale Ag resulted by dint of redox reactions principally involving different phytochemicals like polyphenols, ascorbic acid, capsaicinoids, etc. Dissociation of citric acid also effectively contributed to the procedure by ensuring the presence of required free energy for nanotransformation. Therefore, where microbes like bacteria or fungi want a comparatively longer duration of incubation in the growth media for reducing a metal ion, plant extracts due to the presence of water-soluble phytochemicals perform in a tick. Therefore, in comparison to microbes, cells of the plants are handy and amenable for biosynthesis of inorganic nanoparticles. Similarly, Ag and Au nanoparticles were synthesized using *Cinnamomum camphora* (Armendariz et al. 2004) leaf biomass and broth. Recently, coriander leaf extract (Awwad et al. 2013) and *Cinnamon zeylanicum* bark extract and powder (Rao and Paria 2013) and quite recently *Trianthema decandra* root extract (Singh et al. 2010) were used to biosynthesize Ag nanoparticles. Both coriander and cinnamon are rich in aromatic phytochemicals such as terpenoids like coriandrol and cinnamomum along with cinnamic acid, vitamin C, tannin, and oxalic acid, which are quite labile in negotiating a nanotransformation as found earlier (Chandran et al. 2006) while the roots of *Trianthema* might contain a rich treasure of catechin and hydroxyflavones (Singh et al. 2010). Earlier, nitrogenase-rich *Gliricidia sepium* (Jacq.) was also employed for preparing Ag nanoparticles (Raut et al. 2009). Besides, few papers have recently been poured in showing the formation of different nanomaterials based on the phytochemicals, organic acids, etc. present in the plant and/or plant parts (Jha and Prasad 2013b, 2014b, 2015, 2016a, b). In addition, the trail continues. A general schematic representation along with the generation of free energy in the medium for the various fabrication of inorganic nanoparticles (metal/oxide/chalcogenide) using plant and/or plant parts have been illustrated in Fig. 1.2 considering the above facts.

1.7 Animal Systems

Like other cohorts of nature, animals too require metals to ensure their physiology and metabolism. Once the limit of this requirement exceeds, the system undergoes stress. It is suggested that heavy metals played an important role in the origin of life itself and so have endothermic among birds and mammals (Arruda et al. 1995; Clarke and Pörtner 2010). Nature has its own orchestration against any assault and that is available among animal cohorts. Like other animals, insects also have affiliated to heavy metals as essential elements in their normal metabolism. The preservation of internal homeostasis though is achieved through diffusion regularly but more meaningfully by ameliorating a specific structure called spherocrystals—originating from the ER-Golgi complex where elements precipitate upon a glycosaminoglycan nucleus in a fragile peripheral stratum. Quite a few of the spherocrystals may store compounds of minerals, commonly phosphates, while others may store waste organic chemicals such as urates. Whenever additional metals are abundant in the environment, insects such as cockroaches and ants are apt enough to stay alive and to trap the metals (e.g., Pb or Cd) in the boundary layers of spherocrystals; the chemistry of cytoplasm remains unaltered. Insects seemingly have the vigor to circumvent the high levels of toxic metals probably due to their odd habitats. In addition, lysosomes are aptly able to retain the potentially toxic heavy metals like Cd or Hg within metallothionein-like proteins (Ballan-Dufrançais 2002).

The body walls (exoskeleton) of most of the insects (like cockroach, ants, banana flies or mosquitoes, etc.) are made up of chitin (polymeric *N*-acetylglucosamine). Concurrent presence of both acetyl and amino group itself speaks in volumes regarding adaptive vibes among insects and that becomes a boon while one undertakes the pursuit of any nanomaterial synthesis. The broth behaves mildly acidic and is very amenable towards pH modulation, thereby ensuring any nanomaterial of choice. Further, cockroaches contain the proteins that initiate allergic alerts among humans, identified as tropomyosin. The thermodynamically less studied actin-binding protein controls actin mechanics. It has four woven alpha helices—A, B, C, and D—making a quaternary structure and is responsible for muscle contraction (Asturias et al. 1999). Along with its regular enrapting thermodynamic vibes, this promising protein also provides redial encapsulation to the burgeoning nanomaterials.

Further, a comprehensive collusion of Bla g 2 with the structures of other well-known aspartic proteases suggests that ligand binding could be tangled in the activity of this allergen (Arruda et al. 1995). The loss of balance of metals due to genetic impairments or environmental pollution is a worldwide problem assorted with negative health effects. An exhaustive study uncovered an appreciable number of genes and their regulatory cues tangled in maintaining heavy metal homeostasis involving the metals tested in the study, cadmium, copper and zinc, instigates a wide array of responses and that includes triggering of genes coding for metallothioneins, transporters, glutathione-mediated detoxification pathway components, antimicrobial peptides, ubiquitin conjugating enzymes, heat shock proteins, and cytochrome P450

enzymes. The generic induction of metallothionein by the metals such as copper, zinc, and cadmium is well aligned with their metal scavenger function and protective role against metal toxicity through the downregulation by copper depletion but remarkable disparities in terms of response may arise among metallothionein congeners. MtnA is induced in response to a copper assault, while MtnB and MtnC are more strongly induced by zinc and cadmium, respectively. A recent study noted regarding metallothionein's preference towards different metallic assaults and it was found that MtnA played a crucial defending role against excessive copper, while MtnB got triggered against zinc and cadmium, and other congeners MtnC and MtnD played a sub-ordinative role. So, in complete terms, MtnA elaboration was suggested to be the major hunter of metals at *Drosophila* larval stage (Yepiskoposyan et al. 2006; Egli et al. 2006).

Fish, like other animals, need heavy metals in their metabolism in traces while most of them act as micronutrients for both plants and animals, which are essential constituents of enzymes and hormones that indeed make them indispensable for an array of metabolic reactions. Among fish, transportation of metals occurs through the blood where the metal ions are usually attached to proteins. Further, when metals are brought into contact with different organs and tissues of the fish, they accumulated there (Asturias et al. 1999). Therefore, metals are usually present in high concentrations in the organs like gills, intestines, and digestive glands. Although fish intestines are seldom consumed, it usually accumulates more heavy metals in the study and this might represent good biomonitors of metals occurring in the surrounding environment. Metallothionein genes are triggered under heavy metal assault by specific transcription factor like MTF-1, which attaches to a short DNA sequence known as metal response elements (MREs) (Ayandiran et al. 2009). At the genomic level, as a homolog to the mammalian MTF-1, the expression of MTs is regulated transcriptionally by metal-responsive transcription factor 1 (MTF-1). MTF-1 binds to the short DNA motifs termed metal response elements (MREs), upon metal assault, in the MT promoter, which is quite significant and capable of mediating the transcriptional rejoinder to heavy metals (Selvaraj et al. 2005; Stuart et al. 1984).

Chicken like other animals have blood as carrier where metals usually are attached to proteins. Many heavy metals are used as trace elements and feed additives in poultry feed. These metals are common in our environment, some of these (iron, copper, manganese, zinc, etc.) are essential for good health, however; other (arsenic, mercury, lead, cadmium, etc.) are poisonous and deleterious for health (Jadhav et al. 2007). Arsenic is most important and usually found in the environment in organic and inorganic forms with different bioavailability. Arsenic can compel antibiotic resistance and this is also true among bacteria. There is trend of using arsenic with antibiotics as feed additive among poultry farmers. However, vitamin C is found to partially mitigate the toxicity of arsenic among broiler birds (Suganya et al. 2016). Similarly, lead, mercury, cadmium, etc. could also have annihilating effect on chicken. It was noticed earlier that functionalities of superoxide dismutase (SOD) and catalase (CAT) are enhanced even under sub-acute toxicity of cadmium while the glutathione (GSH) tends to decline appreciably among the erythrocytes of

Cd exposed birds (Yadav and Khandelwal 2006). A recent exhaustive study suggests the role of ascorbic acid (vitamin C) as an anti-stress among poultries (Ahmadu et al. 2016) and it may be due to their role in glutathione metabolism. Recently, two dead lower animals' broth of banana fly (*Drosophila* sp.) and cockroach (*Periplaneta americana*), respectively, were used to synthesize CdS and gold nanoparticles (Jha and Prasad 2012, 2013a), and discards of fish, principally intestines, were taken into use for preparing Ag nanoparticles (Jha and Prasad 2014c) as well as chicken and goat meat processing discards for synthesizing silver and zinc oxide nanoparticles (Jha and Prasad 2016c, 2018) which still harbor promising metabolites that are otherwise wasted by festering. Finally, the cessation of cells tends to liberate the potential metabolites that help in nanomaterial fabrication.

1.8 Thermodynamic Considerations

Proteins are naturally bestowed biological ligands, because they contain amino acids, which act as multidentate chelate ligands, providing an amenable spatial fixation and act as a medium themselves due to defined dielectric properties. Initial works particularly by Hsien Wu and others (Anfinsen 1973; Anfinsen and Scheraga 1975; Edsall 1995) established the concept related to the denaturation of soluble proteins involved in transitions between a relatively compact and tidy structure to a whippier, muddled open chain of polypeptide. Tropomyosin (Tm) was discovered more than 65 years ago (Edsall 1995; Bailey 1946). This actin-binding, coiled protein is an enrapturing biological molecule and its stability, structural and functional properties remain yet to be fully understood (Bailey 1948).

Widely distributed among all eukaryotic cell types it has as many as 40 isomeric forms within an individual cell speaking itself regarding functional prodigality of this protein macromolecule (Perry 2001; Gunning et al. 2008). Enumerable experiments for ascertaining thermodynamic parameters of protein transition rest upon approximation of two states behavior for the system itself. For proteins, the native/ folded may be represented as A, unfolded form may be denoted as U, respectively, and this transition may be temperature and pH dependent or may broadly depend upon the concentration of denaturant. Free energy difference between native and unfolded (ΔG_{unf}) is reported to be in the range of +20 to 60 kJ mol⁻¹. Experimentally, it is noticed that the temperature craving of ΔG_{unf} displays that for most proteins the folded form is, not unreasonably perhaps, most stout in the physiological temperature range. The relatively small amount of free energy of expansion is due to much larger and much more temperature dependent enthalpy and entropy contributions. Massive molecules like tropomyosin principally framed by tightly held random coils, interpenetrated and tangled with each other (Cooper 1999).

Tropomyosin is quite a large biopolymer in comparison to the solvents. These contain very tightly held random coil units, entangled and interpenetrating all through. The degree of cohesive and other forces of attractions are variable between the molecular units and neighboring coils. The molecules of solvents take little time in order to overcome such forces and to liberate the individual units from the

polymeric phase. There lies a clear difference of the procedure of dissolution and a molecule having low molecular weight. The interaction of a polymer molecule with the solvent is an interesting cue of events. The forces of attraction or dispersion commences and emerges between them and at a point solvent–solute interaction overpowers the solute–solute interactions leading to the weakening of the polymer holding forces and subsequently the salvation takes place. This is an overall slow process as the abovementioned interactions take time. The principle of thermodynamics governing dissolution of molecules having high or low molecular weight remains interestingly the same. State functions are quantities that address principally the state of a system and not the procedure or path being taken or followed to reach this state. The quantity V is broadly dependent upon its initial and final value of V , irrespective of the path being used for reaching V_f from V_i . Identically, temperature and pressure are also in the same category. As per the first law of thermodynamics, irrespective of the heat being absorbed or released, a change in internal energy or the work being done on or by the system is not of much significance. The total internal energy of a system is a state function. The transition between one state to another does not involve exchange of heat or work or in other words; heat may or may not be exchanged and work may or may not be done. Therefore, heat and work do not qualify as state functions. However, a change in temperature can be noticed upon absorption of heat but the work done by a system does qualify for the final state. A chemical reaction in solution is being investigated under varied conditions having variable pH, ionic strength and type of solvent, etc. The amount of free energy of activation tends to remain constant or show a tendency towards little change (Holwill and Silvester 1967).

The value of Partial Molar Volume (PMV) remains an important thermodynamic quantity harboring pivotal information regarding solvent–solute interactions along with solute behavior/structure in solvated state. It remains to be the most imperative deal while analyzing the effect of pressure on a defined chemical reaction. The biological sources (cultures, extracts, or broths) are nothing but mere conglomerates of different metabolites, which are released abreast entity due to heat. Bio-legends and metal ions make coordination complexes of broadly biological relevance because metal ions are the sites of Lewis acids capable of accepting lone pairs of electrons donated by the ligand, which behaves as Lewis base. This is well illustrated in metallothionein where 30–35% of its constituent amino acid cysteine carries soft SH-groups. The primordial life activity of metallothioneins is to preserve the cells from assaults of heavy metal toxicity. Secondly, due to a favorable chelate effect, metal chelate complexes are quite stable, because there is always a favorable entropic factor accompanying the release of non-chelating ligands. Similarly, pK_a values of coordinate ligands also play significant role dependent upon tuning of redox potential. Finally, different biopolymers affect the thermodynamic stoutness of a metal center, since it can control, through its three-dimensional structure such as stereochemistry, available ligands for coordination, local hydrophilicity and or hydrophobicity, steric blockage of coordination sites, and hydrogen bonding formation. This enrapturing thermodynamic interaction/ interdependence keeps molecules agile and ensures the formation of nanomaterials is dependent upon the modulation of experimental cues. The mechanism of such nanotransformation

could be understood using the nucleation and growth theory in which the overall free energy change (ΔG) must be overcome. Here the case of spherical nanoparticles is considered. ΔG is the prognostic of sum of the free energy due to the formation of a new volume and new surface being created (Jha and Prasad 2013b; Li et al.

2007): $\Delta G = -\frac{4}{V}\pi r^3 k_B T \ln(S) + 4\pi r^2 \gamma$, where V , r , k_B , S , and γ are the molecular

volume of the precipitated species, radius of the nucleus, Boltzmann constant, saturation ratio, and surface free energy per unit surface area, respectively. It follows from this equation that a decrease in or an increase in S is helpful in the formation of desired/targeted nanoparticles. In a biochemical reaction involving microbe/plant metabolites, the interactions of broth/culture medium with metal salt make the concentration of metal ions surrounded by different metabolites like flavonoids, terpenoids, organic acids, polypeptides, etc. adhered to the metal nuclei that lead to a lower surface energy of the crystal lattice. So far, we can draw this emphatic conclusion that it is the core molecular wealth/metabolites along with the experimental cues, which decide the fate of fabrication of the type of nanomaterial, and the source/mean/method whether it is chemical or biological is oblivious as the crux lies with might of thermodynamics! All these facts have been illustrated in the Fig. 1.3 that clearly delineates the participation of different pivotal factors in the synthetic cue such as energy of decomposition if we opt to take a soft-chemical

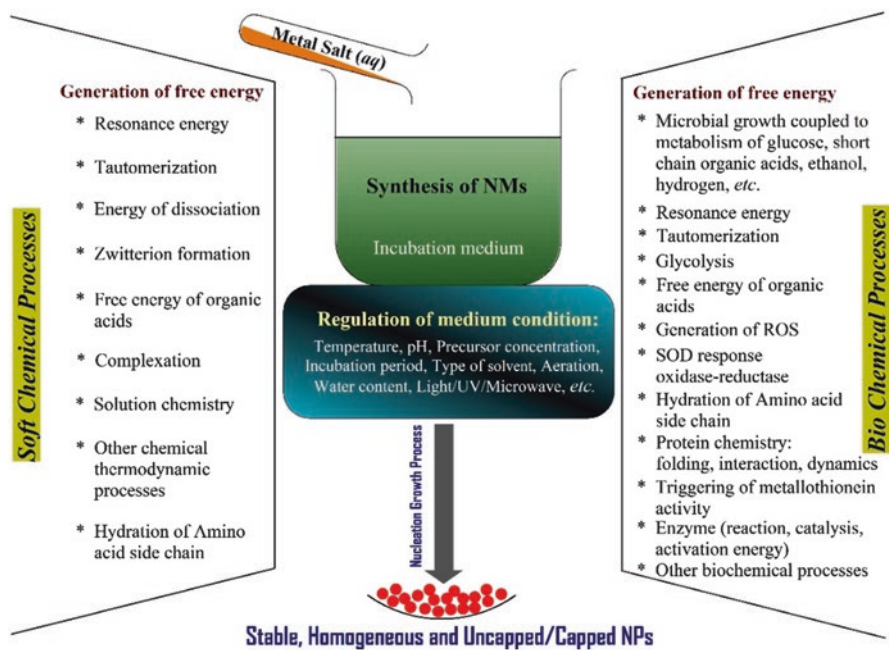


Fig. 1.3 Generation of free energy in the incubation medium for the preparation of different nanomaterials: Comparison between soft-chemical and biochemical methods

route, generation of ROS and subsequent triggering of phytochelatin, metallothionein and GSH along with many other factors leading to a successful nanotransformation.

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Chapter 2

Microbes: Nature's Cell Factories of Nanoparticles Synthesis



Tabeer Khan, Sidra Abbas, Anila Fariq, and Azra Yasmin

2.1 Introduction

Modern science and technology is working on the fabrication of new yet improved nanodevices and systems possible for a variety of industrial, consumer, and biomedical applications. Theoretical application of nanotechnology was first envisioned by a Physicist Richard Feynman in 1959. Recent developments in nanotechnology has led to the synthesis of nanoparticles from biological sources. The prefix “nano” is a Greek word which means “dwarf” very small or miniature size. These nanoparticles were considered as building blocks for the development of optoelectronic, electronics, various chemical and biochemical sensors (Narayanan and Sakthivel 2010; Faraz et al. 2018). Nanoparticles are defined as the small solid particles of one dimension with the average size of 10–1000 nm. Few examples of nanosized biological materials include DNA (2.5nm) and viruses (100nm) (Wagner et al. 1992; Lyubchenko and Shlyakhtenko 1997).

Nanoparticles possesses unique wavelength that is below the wavelength of light, which makes them appear transparent. Thus metal nanoparticles can also be easily attached to the single strand of DNA. Due to these unique properties, they have gained enormous importance to be used in diverse areas such as electronics, cosmetics, coatings, packaging, and biotechnology by controlling and modifying their size shape and physicochemical behavior. Basically, there are two approaches to synthesize nanoparticles: bottom up approach and top down approach. In bottom up approach, basic building blocks were synthesized and assembled into the final nanostructure by chemical and biological procedures. Top down approach starting larger material is reduced into smaller one by physical and chemical means. Major

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drawback of both the approaches is that they require huge amount of energy, toxic chemicals, and formation of hazardous by-products (Thakkar et al. 2009; Prasad et al. 2016). Also physically and chemically synthesized nanoparticles are less biocompatible and due to their toxic nature their use is limited. So there is need to develop ecofriendly and economical method for the synthesis of nanoparticles (Hosseini and Sarvi 2015).

Recently, biological synthesis emerged as an alternative to conventional methods of nanoparticle synthesis. It involves the use of microorganisms and plants for synthesis. Biological entities present on this planet have been in regular touch with its surroundings. Microbes are found to be the small living entities and microbial mediated synthesis of nanoparticles established a new field of research nano-biotechnology. With the passage of time organisms evolve certain mechanisms to alter the chemical nature of toxic metal to survive extreme metal concentrations in environment. So, one can say that nanoparticles are the by-products of reduction mechanisms by organisms (Durán et al. 2007). Microorganisms produce different types of enzymes that are involved in the reduction of toxic and hazardous metals and convert them into nanoparticles. Nanoparticles synthesis through biological entities offers a clean, nontoxic and environmental friendly way with wide range of size, shape, composition, and physicochemical properties (Sastry et al. 2005; Mohanpuria et al. 2008; Prasad et al. 2016). Extensive studies have been conducted on metal bioremediation and metal–microbe interactions but new dimensions in microbial nano-biotechnology research are yet to be explored (Narayanan and Sakhivel 2010).

2.2 Traditional Sources of Nanoparticles Synthesis

Most common mode of nanoparticles synthesis includes physical and chemical methods. Both processes follow two approaches for synthesis of nanomaterial which are top down and bottom up. In bottom up approach, atom and molecular constituents are made up of single molecule. These molecules or atoms are attached via covalent bonding making them far stronger. A lot of information could be stored in devices made from bottom up approach. Chemical and physical techniques that use bottom up approach are AFM, liquid phase techniques based on inverse micelles, sol-gel processing, chemical vapor deposition (CVD), laser pyrolysis, etc. *Top down* method includes synthesis of smaller and smaller particles by using bulk materials. This approach includes cutting, carving, and molding of materials but there is still need to develop highly advanced nanodevices through this process. Methods that follow top down for nanomaterial synthesis include laser ablation, milling, nanolithography, hydrothermal technique, physical vapor deposition, electrochemical method, etc. (Nikalje 2015; Rajput 2015).

Depending on target material to be fabricated, almost every element of periodic table is utilized for nanomaterial synthesis. These nanomaterials have applications

from nanoelectronics to nanomedicines. Nanotechnology revolutionized material manufacturing of desired shape and design without use of machining, metals, polymers, and ceramics. Furthermore it also provides benefits to chemical catalysis from fuel cell to catalytic converters and photocatalytic devices due to their large surface to volume ratio. Some of the examples of physical and chemical methods of nanomaterial synthesis are;

2.2.1 Gas Condensation

To synthesize nanocrystalline metals and alloys gas condensation was used. General process involves vaporization of inorganic or metallic material by thermal evaporation. In this process, ultrafine particle of 100 nm of size is synthesized by gas phase collision (Tissue and Yuan 2003). This method had some limitations such as maintenance of temperature ranges, source-precursor incompatibility, and dissimilar evaporation rates in an alloy. Besides thermal evaporation, alternative techniques such as sputtering electron beam heating and plasma methods were used for production of ultrafine nanoparticles. Variety of clusters of Ag, Fe, and Si were produced via sputtering (Hasany et al. 2012).

2.2.2 Vacuum Evaporation

In vacuum evaporation or deposition and vaporization, compounds to be fabricated are vaporized and deposited in a vacuum. Thermal processes are involved in the vaporization of material at a pressure of 0.1 Pa in vacuum level of 10–0.1 MPa. During vapor phase nucleation atoms are passed through gas where they are collided and fine particles are synthesized of size range from 1 to 100 nm. This method is economical and deposition rate is also high (Winterer et al. 2003).

2.2.3 Chemical Vapor Deposition and Chemical Vapor Condensation

In chemical vapor deposition (CVD) method, chemical deposition vapor or gas phase is converted into solid which in turn deposited onto the heated surface via a chemical reaction. Temperature above 900 °C is required for activation of thermal CVD reaction. Nanocomposite powders had been prepared by CVD. CVC (Chemical Vapor condensation) reactions were proceeded by activation energy generated by several methods. Particles of ZrO₂, Y₂O₃ and nanowhiskers had been produced by CVC method (Konrad et al. 2001; Winterer et al. 2003).

2.2.4 Mechanical Attrition

Mechanical attrition involves synthesis of nanomaterial by structural decomposition of coarser grained structures. Ceramic nanocomposite and magnesium oxide had been fabricated through this method. Mechanical alloying method was advantageous as it can be carried out on room temperature. This process can also be performed on high energy mills, centrifugal type mills, vibratory and low energy type mills (Sharma et al. 2009).

2.2.5 Chemical Precipitation

Formation of nanomaterial by chemical precipitation involved reaction between material and suitable solvent. Size of nanomaterial to be synthesized may be controlled by precipitation, by avoiding the physical changes, and by aggregation of crystals. Surfactants are added to avoid clustering of particles (Konrad et al. 2001; Sharma et al. 2009).

2.2.6 Sol-Gel Methods

Among all the other methods, sol-gel methods are extensively used recently. Precursors for synthesizing colloids are ions of metal alkoxides and alkoxy silanes. Furthermore these colloids are synthesized by a network in continuous liquid phase. Sol-gel process is carried out in four steps which includes hydrolysis, condensation, and growth of particles and agglomeration of particles (Lu and Jagannathan 2002; Morita et al. 2004).

All these methods are robust but not economical, require a lot of energy and a large amount of toxic by-products are generated. To reduce these risks associated with the physical and chemical method of synthesis, focus on less toxic methods is increasing.

2.3 Green Routes of Nanoparticles Biosynthesis

Besides conventional methods of nanoparticles synthesis, increasing amount of research is being performed on the green synthesis of nanoparticles. Green synthesis of nanoparticles utilizes plants and plants extracts which have advantage over other methods as they are nontoxic and possess natural capping or stabilizing agents. Moreover green synthesized nanoparticles have diverse nature, more stability and process is one step procedure. General phenomenon of nanoparticles

biosynthesis include bioreduction of metals upon interaction of plant extracts with metals. Plants metabolites like sugars, terpenoids, polyphenols, alkaloids, phenolic acids, and proteins play an important role in metal ions reduction into nanoparticles (Prasad 2014).

Lot of researches had been conducted on green synthesis of silver and gold nanoparticles. Silver and gold nanoparticles synthesis was carried out by utilizing *Geranium* extract, *Aloe vera* plant extracts, and sundried *Cinnamomum camphora* (Shankar et al. 2004a, b; Chandran et al. 2006; Huang et al. 2007). A homogeneous solution of AgNPs was obtained simply by reacting the *Jatropha curcas* extract with silver nitrate solution. AgNPs obtained were of 10–20 nm in size (Bar et al. 2009). Another inexpensive synthesis of bimetallic Ag and Au nanoparticles had been synthesized with the aid of *Plumeria rubra* plant latex (Patil et al. 2012). As discussed earlier that plant metabolites act as reducing agents in the reduction of metal ions into nanoparticles. Study reported by Christensen et al. (2011) explained the presence of natural reducing agents eugenol and carbazoles in the leaf extracts of *Murraya koenigii* (Christensen et al. 2011). Silver nanoparticles also possess effective antimicrobial property against *Escherichia coli* and *Vibrio cholera* at a concentration of 10 µg/mL (Krishnaraj et al. 2010). Besides silver nanoparticles plant also synthesizes gold nanoparticles. Neem plant, *Azadirachta indica* was utilized for the synthesis of silver, gold, and bimetallic AuAgNPs. Terpenoids and flavanone components of plant seemed to act as stabilizing agents of nanoparticles (Shankar et al. 2004a, b). Similarly leaves of *Mirabilis jalapa* were exploited for the synthesis of gold (Au) nanoparticles (Vankar and Bajpai 2010). Only drawback of plant-based synthesis over microbial synthesis is huge biomass with prolonged synthesis time. Otherwise, it would be a cheap and green synthesis of nanoparticles.

2.4 Mechanisms of Biosynthesis of Nanoparticles

Nanoparticles have attracted attention of the researchers all around the world due to their size ranging from 1 to 100 nm, unusual and captivating properties, and applications in numerous fields (Daniel and Astruc 2004; Kato 2011). There are various methods such as physical, chemical, and biological available for the synthesis of nanoparticles (Liu et al. 2011; Luechinger et al. 2010; Tiwari et al. 2008; Mohanpuria et al. 2008). Among these, physical and chemical methods have gained popularity due to bulk production of nanoparticles in a relatively short period of time. However, due to high costs, use of toxic chemicals, and formation of toxic by-products during their production have limited their use in clinical applications (Bhattacharya and Mukherjee 2008).

Use of enzymes for nanoparticles has reduced the cost of the process as expensive chemicals are no longer required. This method is more acceptable as it is more environmental friendly and not as energy intensive as chemical method (Simkiss and Wilbur 1989; Bhattacharya and Mukherjee 2008). Biological method reduces the detrimental effects produced as a result of physical and chemical methods.

Biosynthesis of nanoparticles has been exploited throughout the world because of its low cost, high efficiency, and nontoxic by-products. Microbes like bacteria, algae, actinomycetes, yeast, and fungi have gained attention of the researchers due to their high adaptability to toxic environment and ability to synthesize nanoparticles at mild temperature, pH, and pressure (Li et al. 2011; Prasad et al. 2016).

2.4.1 Intracellular and Extracellular Biosynthesis

The exact mechanism of nanoparticles using microorganism is not yet fully comprehended because different microorganisms interact differently with the metal ions. Many organisms have the ability to produce nanoparticles from inorganic materials either intracellularly or extracellularly (Mukherjee et al. 2001a, b). However, the mechanism of intracellular or extracellular production is unique to each organism. The intracellular mechanism requires a special ion transport system and cell wall plays important role in this process. During the process there is an electrostatic interaction of positively charged metal ions with the negatively charged cell wall, thereby converting the metal ion into elemental form via various enzymes. The nanoparticles diffuse off through the cell wall (Fig. 2.1). Extracellular biosynthesis of nanoparticles is mediated via enzymes either releases in the growth medium or by enzymes in cell membrane (Fig. 2.2) (Li et al. 2011).

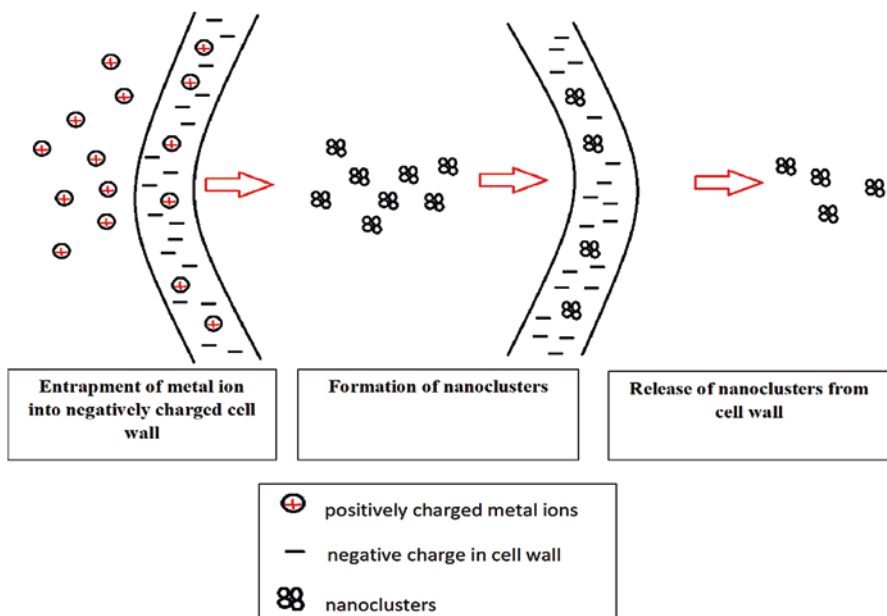


Fig. 2.1 Intracellular synthesis of nanoparticles

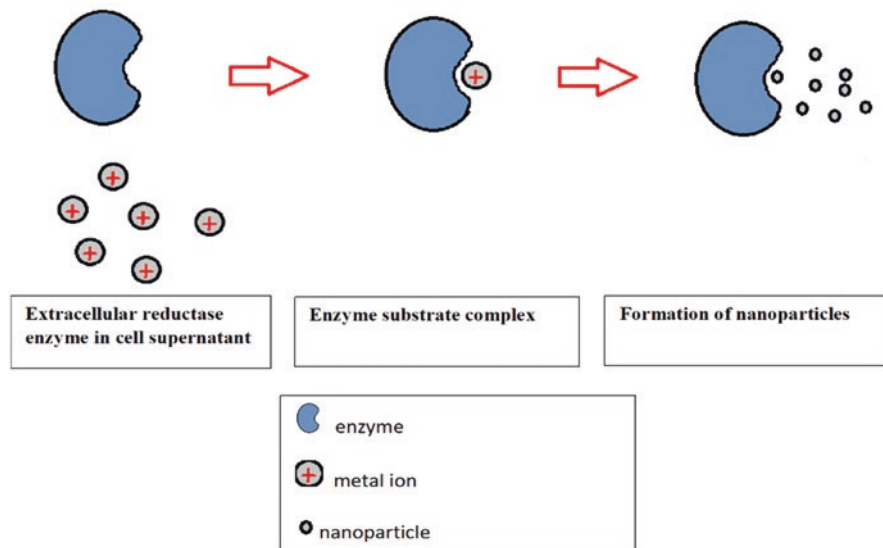


Fig. 2.2 Extracellular synthesis of nanoparticles

2.5 Microbes as Tiny Cell Factories of Nanoparticles Biosynthesis

Biological entities like microbes were exploited for nanoparticles synthesis. Among microbes, bacteria, yeast, and fungi were preferred due to their fast growth rate, easy cultivation and their ability to grow at ambient physiological conditions. A brief overview of microbe mediated synthesis of different nanoparticles has been tabulated in Table 2.1.

2.5.1 Nanoparticles Synthesis from Bacteria

Due to difference in nature/properties of colloidal and bulk solution, gold nanoparticles are synthesized due to their excessive antioxidant potential. Microbial mechanism of gold nanoparticle synthesis involves solubilization to promote oxidation of gold to create ions. To stabilize these gold ions, ligands were secreted by microorganisms to avoid complex formation (Reith et al. 2009). Alkalotolerant *Rhodococcus* sp. was used for the synthesis of monodispersed gold nanoparticles (Ahmad et al. 2003a, b). Ability of high radiation and oxidant resistant bacterium *Deinococcus radiodurans* was explored to synthesize AuNPs. Data suggested that Au(III) may be reduced to Au(I), and further to Au (0) with the capping groups to stabilize the AuNPs (Li et al. 2016).

Table 2.1 Microbial mediated synthesis of different nanoparticles

Microorganisms	Type of nanoparticle synthesized	Size (nm)	References
Bacteria			
<i>E. coli</i>	Cu, Ag	3–9	Ruparelia et al. (2008)
<i>Bacillus subtilis</i>	Cu, Ag	3–9	Ruparelia et al. (2008)
<i>Staphylococcus aureus</i>	Cu, Ag	3–9	Ruparelia et al. (2008)
<i>Vibrio alginolyticus</i>	Ag	50–100	Rajeshkumar et al. (2014a, b)
<i>Bacillus sp.</i>	Ag	65–70	Malarkodi et al. (2013)
<i>Proteus mirabilis</i>	Ag	5–45	Al-Harbi et al. (2014)
<i>Corynebacterium glutamicum</i>	Ag	5–50	Sneha et al. (2010)
<i>B. amyloliquefaciens</i>	Ag	10–100	Behera et al. (2013)
<i>Thermomonospora</i>	Au	50–100	Kasthuri et al. (2008)
<i>Rhodopseudomonas capsulata</i>	Au	10–20	He et al. (2007)
<i>Delftia acidovorans</i>	Au	50	Johnston et al. (2013)
<i>Pseudomonas stutzeri</i>	Cu	11	Varshney et al. (2010)
<i>Pseudomonas fluorescens</i>	Cu	49	Shantkriti and Rani (2014)
<i>Morganella psychrotolerans</i>	Cu	2–5	Ramanathan et al. (2011a, b)
<i>Rhodobacter sphaeroides</i>	CdS	4.3	Bai et al. (2009)
<i>E. coli, Klebsiella pneumoniae</i>	Cd	5–200	Mousavi et al. (2012)
<i>Bacillus licheniformis</i>	Cd	20–40	Shivashankarappa and Sanjay (2015)
<i>Bacillus subtilis</i>	FeO	60–80	Sundaram et al. (2012)
<i>Magnetospirillum</i>	Magnetite	47	Elblbesy et al. (2014)
<i>Klebsiella oxytoca</i>	Magnetite	Not detected	Arçon et al. (2012)
<i>Alcaligenes faecalis</i>	FeSO ₄ , Magnetite	43.60, 12.30	Kaul et al. (2012)
<i>Shewanella oneidensis</i>	Magnetite	40–50	Perez-Gonzales et al. (2010)
<i>Clostridium sp.</i>	Magnetite	2–10	Kim and Roh (2014)
<i>Thermoanaerobacter sp.</i>	Magnetite	13	Moon et al. (2010)
<i>Lactobacillus plantarum</i>	ZnO	7–1	Selvarajan and Mohanasrinivasan (2013)
<i>Aeromonas hydrophila</i>	ZnO	57.72	Jayaseelan et al. (2012)
<i>Pseudomonas sp.</i>	Pd	Not detected	Schlüter et al. (2014)
<i>Bacillus megaterium</i>	Ag, Pb, Cd	10–20	Prakash et al. (2010)
Fungus			
<i>Phanerochaete chrysosporium</i>	Ag	25	Vigneshwaran et al. (2006)
<i>Fusarium oxysporum</i>	Ag, Au	20–50	Vilchis-Nestor et al. (2008)
<i>Mucor hiemalis</i>	Ag	5–15	Aziz et al. (2016)

(continued)

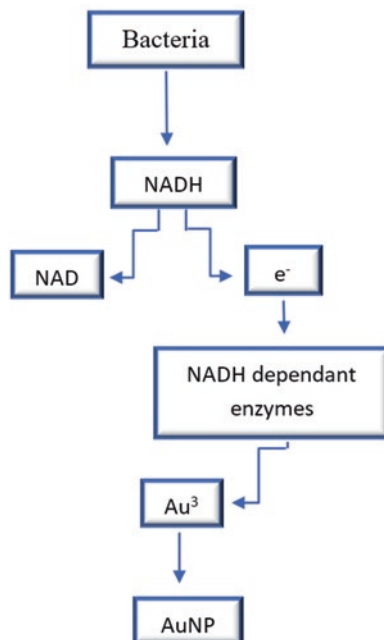
Table 2.1 (continued)

Microorganisms	Type of nanoparticle synthesized	Size (nm)	References
<i>Phanerochaete chrysosporium</i>	Ag	100	Mondal et al. (2011)
<i>Aspergillus flavus</i>	Ag	7–10	Evanoff Jr and Chumanov (2005)
<i>Aspergillus fumigatus</i>	Ag	5–25	Vigneshwaran et al. (2007)
<i>Coriolus versicolor</i>	Ag	350–600	Merga et al. (2007)
<i>Fusarium solani</i>	Ag	5–35	Hu et al. (2008)
<i>Aspergillus terreus</i>	Ag	13.80–20.0	Velhal et al. (2016)
<i>Aspergillus fumigatus</i>	ZnO	1.2–6.8	Raliya and Tarafdar (2013)
<i>Pestalotia</i> sp.	Ag	10–40	Raheman et al. (2011)
<i>Aspergillus oryzae</i>	FeCl ₃	10–24.6	Raliya and Tarafdar (2013)
<i>Aspergillus terreus</i>	Mg	48–98	Raliya and Tarafdar (2013)
Yeast			
<i>Rhizopus oryzae</i>	Au	10	Das et al. (2009)
<i>Candida glabrata</i>	CdS	–	Kowshik et al. (2002)
<i>Yarrowia lipolytica</i>	Au	–	Pimprikar et al. (2009)

Besides gold nanoparticles, different bacterial species are known to produce silver nanoparticles. Saifuddin et al. (2009) reported synthesis of silver nanoparticles from *Bacillus subtilis* with a size of about 5–50 nm. Extracellular synthesis of silver nanoparticles was conducted with five psychrophilic bacteria *Phaeocystis antarctica*, *Pseudomonas proteolytica*, *Pseudomonas meridiana*, *Arthrobacter kerguelensis*, and *Arthrobacter gangotriensis* and two mesophilic bacteria *Bacillus indicus* and *Bacillus cecembensis* (Shivaji et al. 2011). Physiological factors like pH, temperature, and salt concentration play important role in nanoparticle synthesis. *Bacillus* sp. was reported to synthesize silver nanoparticle with 1 mM silver nitrate, room temperature within 24 h (Das et al. 2014). Along with environmental factors extracellular enzymes were recognized in biological synthesis. Activity of nitroreductase in bioreduction of silver was studied in *Enterobacteriaceae* and *K. pneumoniae*. Overall reaction was quite fast and within few minutes of silver metal exposure to organisms; silver nanoparticles were synthesized (Mokhtari et al. 2009). Bacteria also possess ability to utilize other metal nanoparticles like *E. coli* (Singh et al. 2010), *M. psychrotolerans* and *M. morgani* (Ramanathan et al. 2011a, b), *Pseudomonas* sp. (Majumder 2012) and *Pseudomonas stutzeri* (Varshney et al. 2010), *Serratia* (Hasan et al. 2008), *Streptomyces* (Usha et al. 2010) had reported for the synthesis of copper nanoparticles. A bacterial synthesis mechanism is illustrated in Fig. 2.3, as an example.

About one-third of the consumer product market utilized metal oxide nanoparticles which possessed wide range of applications (Maynard et al. 2006). These oxide nanoparticles had small size and high density which is why they have different physical and chemical properties. As per their unique physicochemical proper-

Fig. 2.3 Bacterial extracellular synthesis of gold nanoparticle



ties, oxide nanoparticles have wide applications in different industries including synthesis of biosensors, ceramics, absorbents, and/or catalysts (Garcíaa and Rodriguezb 2007). Biosynthesis utilizing bacterial species gained much interest due to low cost, easy reproducibility, and confined particle size. In biological system, extracellular enzymes possess great redox potential. The potential of producing reducing agents helps microorganisms to reduce metal ions into nanoparticles (Baker and Tatum 1998). Biosynthesis of zinc oxide nanoparticles had been reported in numerous researches as simple and low-cost procedure. As antibacterial and anti-fungal agent zinc oxide nanoparticles gained much interest in preparation of personal care products. Studies reported the bacterial mediated synthesis of zinc oxide nanoparticles using *Aeromonas hydrophila* and *Acinetobacter schindleri* along with their antimicrobial activities (Jayaseelan et al. 2012; Busi et al. 2016).

Some oxide forms of metal nanoparticles are difficult to synthesize like copper oxide due to its excessive susceptibility to oxidation. So, to cope with this problem biological synthesis of copper nanoparticles gained much importance. As in case of bacterial synthesis, oxidation of copper nanoparticles was prevented by presence of thiol group which act as capping agent. Biosynthesis of copper nanoparticles offers unique optical, electrical, and antimicrobial applications (Yang et al. 2006; Hasan et al. 2008). Kirthi et al. (2011) reported *Bacillus subtilis* mediated biosynthesis of titanium oxide nanoparticles with an average size of 66–77 nm.

Apart from oxide nanoparticles, sulfide nanoparticles had great appliance in applied research due to their novel electronic and optical properties. These are used in the synthesis of quantum dot fluorescent biomarkers and as cell labeling agents, etc. (Yang and Holloway 2004). *Desulfobacteraceae* and *Rhodobacter sphaeroides* synthesized zinc sulfide nanoparticles with the average size of 2–8 nm and spherical in shape (Labrenz et al. 2000; Bai et al. 2006). Similarly, *Escherichia coli* and *Rhodopseudomonas palustris* were reported for the synthesis of cadmium sulfide nanoparticles with crystalline structure (Sweeney et al. 2004; Bai et al. 2009). Biologically synthesized nanoparticles had been stabilized by the capping of biomolecular compounds. Cadmium sulfate synthesized by the marine bacteria was capped by biomolecular compounds that were involved in the reduction of cadmium sulfate to sulfide nanoparticles. They also hold significant antimicrobial potential against pathogenic bacteria (Rajeshkumar et al. 2014a, b).

With the emerging trend in use of fluorescent biological labels, semiconductor nanocrystals had been widely used for the purpose. Biological cadmium nanocrystal was synthesized utilizing *E. coli* (Rozamond et al. 2004). Bacteria synthesize greater nanocrystals in stationary phase probably due to the presence of lipids and polyphosphates as capping agents that stabilized the synthesized nanostructure (Blattner 1996; Rao and Kornberg 1996). *Serratia marcescens* was capable of synthesizing antimony sulfide nanoparticles. The transmission electron micrograph of the nanoparticles revealed that they were small, regular, and non-aggregated particles with size less than 35 nm (Bahrami et al. 2012). On the other hand, mercury is the highly toxic metal accumulated in the environment through anthropogenic activities. Microorganisms detoxify mercury through their metabolic processes and convert it into nontoxic form. Mercuric nanoparticles were biosynthesized using *Enterobacter* sp. Uniform sized intracellular mercury nanoparticles were synthesized at alkaline pH and with lower concentration of mercury (Sinha and Khare 2011). Another bacterium *Bacillus cereus* MRS-1 isolated from industrial effluents was assessed for its potential to produce mercury sulfide nanoparticles. Strain extracellularly synthesizes mercury sulfide nanoparticles with the size range (10–100 nm) (Sathyavanthi et al. 2013). *Bacillus megaterium* obtained from north Bihar, India, could synthesize silver, lead, and cadmium nanoparticles (Prakash et al. 2010).

There is an emerging development of luminescent quantum dots and semiconductors for biological detection and cell imaging. Bacterial species *Clostridium thermoaceticum* had the ability to precipitate CdCl_2 in to CdS in the presence of cysteine hydrochloride at the surface of cell as well as in the medium (Cunningham and Lundie 1993). Another study reported use of *E. coli* for synthesis of CdS nanocrystals using cadmium chloride and cadmium sulfide with a size distribution of 2–5 nm. Nanocrystal formation not only depends on genetic conditions but also on physiological conditions as evidenced by *E. coli*. CdS nanocrystal formation increases 20-fold when in stationary phase as compared to late logarithmic phase (Sweeney et al. 2004). In the biofilm overriding *Desulfobacteraceae* family, spherical ZnS (Sphalerite) particles (2–5 nm) were synthesized (Labrenz et al. 2000).

2.5.2 Nanoparticle Synthesis from Fungus

Compared to bacteria, fungi have an advantage in large-scale production as it produces large amounts of enzymes involved in silver nanoparticle synthesis (Prasad et al. 2016; Aziz et al. 2016). Moreover, fungal culture is simpler to grow both in the laboratory and at industrial scale. Many fungal species were exploited for the synthesis of silver nanoparticles. Biosynthesis of silver nanoparticle from filamentous fungi *Verticillium* sp. and different species of *Fusarium* was utilized (Mukherjee et al. 2001a, b; Ahmad et al. 2003a, b; Durán et al. 2005). Most of the fungal species produce naphthoquinones and anthraquinones, which act as reducing agents (Siddiqi and Husen 2016). Also enzymes like nitroreductases were involved in the bioreduction of metals. Nitrate reductase is essential for ferric ion reduction to iron nanoparticles (Durán et al. 2005). To identify the possible mechanism involved in nanoparticle synthesis via fungus, different enzymes and metabolites were analyzed. In this regard α -NADPH-dependent nitrate reductase produced by *Rhizopus stolonifer*, as well as phytochelatin, was utilized to form silver NPs successfully (Binupriya et al. 2010). Another report also suggested the possible mechanism of bioreduction from *F. oxysporum* of H₂PtCl₆ and PtCl₂ into platinum NPs by means of a filtered hydrogenase enzyme (Govender et al. 2009).

Vast majority of researches were performed with silver and gold nanoparticles but a little is known about the biological synthesis of platinum NPs. Intracellular or extracellular mode of synthesis and effect of environmental conditions on synthesis of platinum nanoparticles were explored using fungal species *Neurospora crassa* and *F. oxysporum*. *N. crassa* utilized intracellular pathway while *F. oxysporum* follows extracellular pathway of synthesis (Riddin et al. 2006; Castro-Longoria et al. 2012). Similarly *F. oxysporum* was exploited for the synthesis of different sulfide nanoparticles. Studies showed that fungus could synthesize cadmium sulfide (CdS), lead sulfide (PbS), zinc sulfide (ZnS), and molybdenum sulfide (MoS) nanoparticles, when the appropriate salt is added to the growth medium (Ahmad et al. 2002).

Potential application of nanoparticles synthesized from fungal species was limited due to their pathogenicity towards humans. Antimicrobial activity of fungal mediated silver NPs was evaluated against certain bacterial and fungal pathogens (Jaidev and Narasimha 2010; Musarrat et al. 2010). *Rhizopus oryzae* mediated synthesized nano gold bio-conjugate was utilized as antimicrobial agent against pathogenic bacteria such as *P. aeruginosa*, *E. coli*, *B. subtilis*, *S. aureus*, *Salmonella* sp. and the yeasts *S. cerevisiae* and *C. albicans* (Das et al. 2009).

2.5.3 Nanoparticles Synthesis from Yeast

Various studies had revealed the ability of yeast to accumulate significant amount of heavy metals. This characteristic was further explored by the researchers for production of nanoparticles either by intracellular or extracellular enzymes. Due to ease of handling and mass production at laboratory scale, yeast had more advantage

over bacterial mediated synthesis of nanoparticles. Metallic nanoparticles were synthesized by investigating different yeast strains. Silver nanoparticles were synthesized using yeast strain which possess good antimicrobial activity (Kumar et al. 2011). Silver-tolerant yeast strain MKY3 was utilized for extracellular synthesis of silver nanoparticles. Nanoparticles obtained were hexagonal in shape with 2–5 nm in size (Kowshik et al. 2003). *Yarrowia lipolytica* mediated synthesis of gold nanoparticles showed that nanoparticles synthesized were of varying shape. Varying salt concentrations are used to effect the size of NPs (Pimprikar et al. 2009). Similarly *Schizosaccharomyces pombe* was exploited to study the synthesis of CdS NPs and its route intracellular or extracellular pathway of synthesis (Dameron et al. 1989; Kowshik et al. 2002; and Krumov et al. 2007). Along with yeast *Hansenula anomala* amine-terminated polyamidoamine dendrimer as stabilizer was added to aid the synthesis of gold nanoparticles (Kumar et al. 2008). Extracellular synthesis of silver and gold nanoparticles was performed by using *Saccharomyces cerevisiae*. Few examples of nanosized biological materials include DNA (2.5nm) and viruses (100nm) (Lim et al. 2011). Similar finding was obtained when *Candida guilliermondii* was used for synthesis of silver and gold NPs. These nanoparticles also possess significant antimicrobial activity against bacterial pathogen *S. aureus* (Mishra et al. 2011).

2.5.4 Nanoparticles Synthesis by Algae

Green alga *Chlorella vulgaris* was successfully investigated for the production of gold nanoparticles. Gold was bound to algae upon addition of dried algal cell suspension to hydro-tetrachloro-aurate supplemented solution. The rate and amount of gold bound to algal cell was increased with time (Hosea et al. 1986). Three cyanobacteria *P. valderianum*, *P. tenue*, *M. chthonoplastes* and four green algae *R. fontinale*, *U. intestinalis*, *C. zeylanica*, *P. oedogoniana* were screened to their gold nanoparticle production after exposing to hydrogen tetrachloro-aurate supplemented medium. It was observed that all three cyanobacteria were able to produce intracellular gold nanoparticles. Whereas, among four green algae, *R. fontinale* and *U. intestinalis* were able to produce intracellular gold nanoparticles. X-ray diffractometry showed that gold metal ions were successfully reduced. Sizes and shapes of nanoparticles were observed using transmission electron microscopy, and UV-Vis spectrometry. At pH 9 and 7 *P. valderianum* produced hexagonal, triangular, and spherical gold nanoparticles. At acidic pH 5 gold nanorods and spheres were produced by *P. valderianum*, so selection of algae is important as not all species have the ability to produce nanoparticles (Parial et al. 2012). Filamentous cyanobacterium *Plectonema boryanum* was successfully used for biosynthesis of Ag nanoparticles in solution supplemented with silver nitrate at 25 °C (Lengke et al. 2007). In another study, rapid extracellular production of gold nanoparticles was achieved by marine *Sargassum wightii* (Singaravelu et al. 2007). Aziz et al. (2014, 2015) also revealed that Ag nanoparticles synthesized from *Scenedesmus abundans* and *Chlorella pyrenoidosa* could be used as antimicrobial agents.

2.5.5 Nanoparticle Synthesis by Actinomycetes

Like other microorganisms, actinomycetes and yeast are also well known for synthesis of nanoparticles. However, secondary metabolites resulting from actinomycetes are comparatively less explored for synthesis of metal nanoparticles. There are several studies indicating actinomycetes as suitable candidates for intra- as well as extracellular biosynthesis of metal nanoparticles. Actinomycetes produced stable nanoparticles effective against many pathogens (Golinska et al. 2014). Silver nanoparticles were produced intracellularly by actinomycetes as a result of electrostatic bonding between silver ions to the negatively charged carboxylic group of enzymes located on the mycelia wall. Enzymes present in the cell wall reduce the silver ion into silver nuclei. These silver nuclei accumulate together into silver nanoparticles. Intracellular synthesis occurs on the surface of the mycelia due to the electrostatic binding of Ag^+ ions to the negatively charged carboxylate groups in the enzyme present on the cell wall of mycelia. The Ag^+ ions are then reduced by the enzymes in the cell wall forming silver nuclei. The accumulation of the silver nuclei leads to formation of nanoscale silver particles (Sunitha et al. 2013). In another study, *Streptomyces* species was used to synthesize metal oxide nanoparticles extracellularly. Zinc nitrate was readily reduced to nanoparticles when exposed to *Streptomyces* species. This reduction was most likely due to reductase enzyme.

2.6 Advantages of Microbes over Other Routes for Synthesis of Nanoparticles

Besides conventional methods nanoparticles synthesis by using microorganisms gained much interest due to their small size, safe to use, ecofriendly, and economical. Biological methods of nanoparticle synthesis follow single step process, thus eliminating the ruthless physiological conditions. Most of the microbes use their physiological condition, like pH, temperature, etc. for synthesis of nanoparticles. Due to incredible properties, microbial synthesized nanoparticles have turned into noteworthy in many fields in the recent years, such as energy, health care, environment, and agriculture.

2.7 Applications

2.7.1 Microbial Nanoparticles in Agriculture

Phytopathogens are one of the major causes of crop diseases. Biologically synthesized silver nanoparticles act as strong fungicidal against these phytopathogens and control spread of plant diseases (Abd-Elsalam and Prasad 2018). Fungicidal activity of biologically synthesized silver nanoparticles was assessed in various researches

which could be beneficial in protecting plants against these pathogens (Jaidev and Narasimha 2010; Mala et al. 2012; Gopinath and Velusamy 2013; Mishra et al. 2014). Biologically synthesized silver and gold nanoparticles had promising applications in life sciences but very little research had been conducted on their applications in agriculture. Mishra and coworkers synthesized silver nanoparticles using *Stenotrophomonas* sp. with the size of 12 nm. Antifungal effect and inhibitory effect of AgNPs on conidial germination were observed. Furthermore reduced sclerotia germination, phenolic acids induction, altered lignification, and H₂O₂ production were observed which could be the possible mechanisms providing protection to chickpea against *Sclerotium rolfsii*. So these biologically synthesized silver nanoparticles could possibly be used in crop protection (Mishra et al. 2017). Another study reported to check the effect of *Aspergillus fumigatus* mediated ZnO NPs cluster bean (*Cyamopsis tetragonoloba* L.) germination and phosphorous mobilizing enzymes. After application of ZnO NPs, improvement in cluster bean biomass, shoot length, root length, root area, chlorophyll content, total soluble leaf protein, rhizospheric microbial population, acid phosphatase, alkaline phosphatase, and phytase activity was observed (Raliya and Tarafdar 2013). These findings suggest that nanoparticles synthesized from microorganisms could potentially be used in agriculture sector to protect plant against phytopathogens and to enhance the germination of plants (Prasad et al. 2014, 2017a). Further research in this field is required to strengthen the findings.

2.7.2 Microbial Nanoparticles in Environment

Large amount of industrial and agricultural waste is discarded in environment each year which is toxic for human and animal consumption/health (Sangeetha et al. 2017a, b, c). Bio-nanoparticles can also be utilized for environmental remediation. For degradation of organic compounds, microbial based nanoparticles have successfully been utilized. Bacterium *Clostridium* was reported to successfully reduce palladium, Pd (II) ions to form metallic Pd nanoparticles. They efficiently degrade organic azo dyes, methyl orange, and Evans blue. This method could be used as alternative to conventional waste water and ground water treatment (Johnson et al. 2013). In conventional methods for synthesis of nanomaterials like quantum dots, a lot of energy, elevated temperatures and pressure is required while biological synthesis has more advantage over conventional methods. Highly luminescent quantum dots of CdS could be synthesized at room temperature from fungus *Fusarium oxysporum* (Kumar et al. 2007). Quantum dots synthesized by conventional methods were used for the detection of pathogenic bacteria in the environment (Zhu et al. 2004). These quantum dots had applications in biomedical research, while their applications in environmental research are emerging. Mono dispersed and different sizes of nanoparticles could be synthesized by fungal species *Fusarium oxysporum*, *Aspergillus fumigatus*, and *F. semitectum* (Dhillon et al. 2012; Shedbalkar et al. 2014).

2.7.3 Microbial Nanoparticles in Biomedicine

(a) Antimicrobial Activity

Concerns over antibiotics resistance focused the researcher to identify alternate methods. Promising alternative is use of silver which is known for its antimicrobial activities (Goodman et al. 2013). Silver nanoparticles can change the functional properties such as solubility and surface adhesion property of bacteria more difficult (Campoccia et al. 2013, Romanò et al. 2013). The synthesis and antimicrobial activity of cadmium sulfide and zinc sulfide nanoparticles against oral pathogens was tested. Size of CdS is from 10 to 25 and that of ZnS was 65 nm. During formation of sulfide nanoparticles, proteins which contain amine groups played their role in reduction process. The antimicrobial activity assessed against oral pathogens such as *Streptococcus* sp., *Staphylococcus* sp., *Lactobacillus* sp., and *Candida albicans*, confirmed microbicidal activity of sulfide nanoparticles (Malarkodi et al. 2014). Fungus *Trichoderma viride* was used to produce silver nanoparticles. Silver metal ions were reduced to stable nanoparticles ranging in size from 5 to 40 nm. Antimicrobial activity of these nanoparticles along with antibiotics was assessed against variety of Gram negative and Gram positive bacteria. It was observed that silver nanoparticles increased the efficiency of ampicillin, kanamycin, erythromycin, and chloramphenicol. It could be concluded that antibiotics along with nanoparticles have better antimicrobial activity (Fayaz et al. 2010; Aziz et al. 2016). Textile fabric fused with silver nanoparticles from fungi *Fusarium oxysporum* can be used as anti-infection agent against pathogens such as *S. aureus* (Durán et al. 2007).

(b) Drug Delivery System

Due to small size, nanoparticles have shown to be an excellent candidate for drug delivery to the target as they can easily surpass the blood–brain barriers and epithelial joints of the skin. Moreover, their increase surface to volume ratio showed better distribution, and as a result of their high surface area to volume ratio, nano-carriers have shown improved distribution of the particular drug exhibiting maximum therapeutically impact (Häfeli et al. 2009; Prasad et al. 2017b).

In a study biocompatibility of magnetic nanoparticles Fe_3O_4 and Fe_2O_3 from *Magnetospirillum gryphiswaldense* was explored. It was concluded that magnetosomes can be used as carrier for novel drug or gene at the cancer tissue sites in hyperthermia cancer therapy, medical imaging such as MRI, and investigation of DNA (Xiang et al. 2007).

Felfoul and fellow researchers studied drug delivery to the target site using magnetotactic bacteria (MTB) with magnetosomes. They used magnetotaxis to change to course of the bacteria and its flagella to direct it in the blood vessels was also used as drug delivery agent (Felfoul et al. 2007). Another group of researchers reported utilization of magnetotactic bacteria nanoparticles (MTB-NPs) for delivering gene to the target site. PEI-associated MTB-NPs were successfully employed to deliver β -galactosidase plasmids both in vitro and in vivo. They managed to use PEI-associated MTB-NPs to deliver

β -galactosidase plasmids, at both in vitro and in vivo levels (Xie et al. 2009). Drug and gene delivery potential of gold nanoparticles over conventional carriers has been explored. Study suggested that gold nanoparticles can be used as drug or gene carriers (Giljohann et al. 2010).

(c) As Anticancer Agents

Cancer is one of the leading causes of death per year all over the world. Conventional methods of treatment of cancer involve surgery followed by chemotherapy/radiotherapy, which had a lot of side effects. Early diagnosis and targeted drug delivery to eliminate the risk of other organ failure is still not well developed. So, nanotechnology offers better alternative in cancer treatment with the development of nanomedicine (Fariq et al. 2017). Silver nanoparticles were extensively studied as potential antimicrobial agents and disinfectants. Recently silver nanoparticles have been used as anticancerous agents. Gurunathan et al. (2013) reported that AgNPs inhibited the growth of human breast cancer MDA-MB-231 cells through activation of lactate dehydrogenase, caspase-3, generation of reactive oxygen species that lead to induction of apoptosis (Gurunathan et al. 2013). MCF-7 breast cancer cells were treated against AgNPs and their cytotoxicity confirmed the possible pathway of induction of apoptosis. These silver nanoparticles inhibit Bcl-2 and activate Bax which further induce cytochrome C release from mitochondria and in turn induce apoptosis (Kulandaivelu and Gothandam 2016). Beside silver nanoparticles, other metal nanoparticles also possess anticancerous activity such as selenium. Selenium nanoparticles from *Streptomyces bikiniensis* had anticancer property against MCF-7 and Hep-G2 human cancer cells. They induce cell death by mobilization of chromatin-bound copper which in turn generate oxidized species resulted in apoptosis of cells (Ahmad et al. 2015). Further study on immune response and toxicity of biologically synthesized nanoparticles prior to commercialization and their application in cancer diagnosis and treatment is desired.

2.7.4 Microbial Nanoparticles in Biotechnology as Biosensors

Nanoparticles having unique optical and electrochemical feature are best suited for use in biosensor devices. Nanoparticles have appealing optical and electronic features and can be utilized in biosensor applications (Faraz et al. 2018). Zheng and coworkers used gold-silver alloy nanoparticles produced extracellularly by yeast in construction of vanillin biosensors. It was concluded that electrochemical response increased many times in Au-Ag alloy based vanillin biosensors. This modified vanillin sensors were efficacious in determination of vanillin from variety of vanilla samples (Zheng et al. 2010).

Bacillus subtilis was used to produce selenium nanoparticles. Nanoparticles produced were of spherical shape with size ranging from 50 to 400 nm. These selenium nanoparticles after 24 h at room temperature were transformed to one-dimensional structure. It was suggested that selenium nanoparticles have the potential to be used

as enhancing and settled material in production of horseradish peroxide biosensor. Prasad and coworkers successfully used microbial selenium nanoparticles from *Bacillus pumilus* sp. for the synthesis of H₂O₂ biosensor (Wang et al. 2010; Prasad et al. 2015).

2.8 Challenges and Future Prospects

Biosynthesis and potential applications of microorganism-based nanoparticles have been focus of researchers for past several years with incredible developments in this field. However, need of the hour is to improve the efficiency of synthesis as nanoparticles synthesized from microorganisms require long incubation/contact time from several hours to sometimes days compared to physical and chemical processes. Particle size, its morphology and mono-dispersity are vital in nanoparticle synthesis and also important challenges, frequently encountered by researchers which require further investigation. It was observed in several studies that nanoparticles formed from microorganisms undergo decomposition or lose stability after sometime. There is a need to focus on stability of the nanomaterials produced biologically. Focus to optimize conditions for large-scale production of nanoparticles at industrial level is also necessary. Genomic and proteomic analysis is another focus point, which will provide the insight about the possible genetic pathways involved in the reduction process. By altering the genetic and proteomic pathways, time span and amount of synthesis may be enhanced.

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Chapter 3

Myco-Nanoparticles: A Novel Approach for Inhibiting Amyloid- β Fibrillation



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3.1 Introduction

The requirement of eco-friendly and green technology in the area of material science is of a great interest due to its distinct biological applications. “Nanotechnology” belongs to one of the imperative areas of modern material science due to its key importance in the development of drug delivery, gene therapy, antibacterial agents, electronics, magnetic resonance imaging, and separation science, to name a few (Sonvico et al. 2005; Wilkinson 2003; Nie et al. 2007). Therefore, the advancement in the synthesis of nanoparticles with varying shape, size, chemical composition, and morphology is indispensable. There are various protocols described for the synthesis of different types of nanoparticles such as chemical, physical, biological, and hybrid methods (Mohanpuria et al. 2008; Luechinger et al. 2009). The synthesis of nanoparticles via chemical and physical channel has gained a huge attention recently (Iravani et al. 2014). However, these methodologies are complicated, expensive, and

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require the use of different types of toxic reagents resulting in restricted biomedical applications. As a result, there is a considerable and urgent need for nontoxic, reliable, eco-friendly, and “green” route techniques for the synthesis of such nanoparticles, especially for biomedical applications. In order to achieve this, the utilization of biological methods using different microorganisms for the synthesis of nanoparticles has emerged as a unique field of research (Li et al. 2011; Prasad et al. 2016). Based on the site of synthesis of nanoparticles by the microorganisms, the process can be classified into two types: intracellular and extracellular synthesis (Talham 2002). The intracellular synthesis is defined as the transportation of metal ions (building block of respective nanoparticles) in the presence of enzymes into the microbial cell (Otari et al. 2015). However, when the metal ions are absorbed at the surface of the microbial cell, forming nanoparticles, it is known as extracellular synthesis of nanoparticles (Zhang et al. 2011). In the following sections, we have described in detail the biological modes for the synthesis of different metallic nanoparticles.

3.2 Biosynthesis of Nanoparticles Using Microorganisms

3.2.1 Gold Nanoparticles (AuNPs)

Michael Faraday for the first time observed that the colloidal gold solutions have different properties from bulk gold (Stephen and Macnaughton 1999). The synthesis of different dimensions (1D, 2D, and 3D shapes) and hollow structures of AuNPs offers an imperative biological application (Kowalczyk et al. 2010). AuNPs are the nontoxic carriers in the area of gene and drug delivery (Ghosh et al. 2008). Their ability to interact with thiol group offers a selective means of controlled intracellular release. The extracellular synthesis of AuNPs has been reported using *Fusarium oxysporum* (fungus) and *Thermomonospora* sp. (actinomycete) (Southam and Beveridge 1996). Moreover, the intracellular synthesis of AuNPs by fungi *Verticillium* sp. has been reported by the same group (Beveridge and Murray 1980). The bacterium *Rhodopseudomonas capsulata* was also used for the synthesis of the AuNPs with different shapes and sizes by modulating the pH (Zhou et al. 2007). The alkalotolerant actinomycete (*Rhodococcus* sp.) has also been reported in the intracellular synthesis of AuNPs (Ahmad et al. 2003b). Alkalotolerant *Rhodococcus* sp. has been known to produce AuNPs under alkaline conditions (Klaus et al. 1999). Nanocrystals and nanoalloys synthesis has been reported using *Lactobacillus* (Mukherjee et al. 2001). The synthesis of AuNPs with distinct shapes (cubic, spherical, and octahedral) has been reported from filamentous cyanobacteria (Klaus-Joerger et al. 2001). Synthesis of AuNPs from blue green alga *Spirulina platensis* has also been reported recently (Suganya et al. 2015).

3.2.2 Silver Nanoparticles (AgNPs)

Silver nanoparticles are gaining significant attention due to their potent antibacterial activity against Gram-positive and Gram-negative bacteria (Fayaz et al. 2010; Aziz et al. 2014, 2015). They have also been reported to possess anticancer and antioxidant properties (Mohanta et al. 2017). AgNPs are capable of physical interaction with the cell surface of various bacteria (Dakal et al. 2016). Studies have reported that AgNPs can break the cellular membranes of microorganisms which further results in an enhanced anti-microbial activity (Franci et al. 2015). The synthesis of AgNPs by bacteria has been shown to be influenced by silver-resistant genes, *c*-type cytochromes, cellular enzymes (nitrate reductase), peptides, and reducing cofactors (Hamedi et al. 2017). The synthesis of the AgNP film from fungi such as *Fusarium oxysporum*, *Verticillium*, *Aspergillus flavus*, or *Mucor hiemalis* has been demonstrated by various workers (Ahmad et al. 2003a; Bhainsa and D'souza 2006, Aziz et al. 2016). AgNPs synthesis using aqueous extract of the seaweed *Sargassum muticum* has also been reported recently (Madhiyazhagan et al. 2015). Another study has reported that when *Pseudomonas stutzeri* AG259 bacterium was kept in the concentrated aqueous solution of silver nitrate, it led to the reduction of the Ag⁺ ions and subsequently the formation of AgNPs in the periplasmic space of the bacteria (Pugazhenthiran et al. 2009).

3.2.3 Alloy Nanoparticles

Alloy nanoparticles are of enormous interest for in situ applications due to their flexible properties (Oezaslan et al. 2011). Alloy nanoparticles are contributing to different fields of science and technology such as optical materials, catalysis, electronics, and coatings (Cortie and McDonagh 2011; Ferrando et al. 2008). An alloy nanoparticle of gold and silver has been used for the catalytic reduction of methylene blue (Tripathi et al. 2015). *Trichoderma harzianum* has been used as a stabilizing and reducing agent in the synthesis of gold-silver alloy (Tripathi et al. 2015). *F. oxysporum* has been used for the synthesis of gold and silver alloy (Senapati et al. 2005). The biosynthesis of alloy of gold and silver nanoparticles under microwave irradiation by their metal precursors and *Jasminum sambac* leaves extract has also been illustrated earlier (Yallappa et al. 2015). Another study has demonstrated the synthesis of gold and silver alloy nanoparticles using yeast cells via extracellular routes (Zheng et al. 2010). The synthesis of gold and silver alloy nanoparticles from fungal strain *Fusarium semitectum* was also reported which was demonstrated to be stable for many weeks (Sawle et al. 2008).

3.3 Nanoparticles Synthesis Using Fungi

As compared to various other groups of microorganisms, fungi are an important group of microorganisms responsible for the synthesis of large amount of metal nanoparticles (Syed et al. 2013; Aziz et al. 2016). This could be due to their capability of synthesizing monodisperse nanoparticles with well-defined shape and size (Mukherjee et al. 2002). Fungal strains consist of large number of enzymes and proteins facilitating the formation of nanoparticles; moreover, these strains are also easy to handle (Mohanpuria et al. 2008; Prasad et al. 2016). A study has reported wherein fungus *Verticillium luteoalbum* was used to synthesize gold nanoparticles using extracellular enzymes (Gericke and Pinches 2006). Another study has reported the synthesis of silver nanoparticle when fungus *Aspergillus niger* was incubated with silver nitrate solution (Gade et al. 2008). The enzymes and proteins produced by fungus facilitated the stability of nanoparticles, as reported in that study. The nanoparticles were shown to have a size distribution between 5 and 25 nm and were monodispersed in nature. In another study, *Fusarium oxysporum* was also used to synthesize CdS nanoparticles (Shakibaie et al. 2010). The authors concluded that the release of reductase enzymes in the presence of *F. oxysporum* led to the formation of CdS nanoparticles. *Aspergillus fumigates* is another fungal strain known for synthesis of metal nanoparticles at wide level (Bhainsa and D'souza 2006). The presence of reductase enzymes facilitates the biosynthesis of metal nanoparticles of different chemical compositions (Adelere and Lateef 2016). Mukherjee *et al.* have reported the synthesis of gold nanoparticles by the intracellular reduction of metal ions in *Verticillium* sp. (Mukherjee et al. 2001). Another study reported the biosynthesis of Ag, Au, Zn, and, Ag-Au nanoparticles using fungi *Volvariella volvacea* (Philip 2009). Another species *Trichothecium* sp. was used for the biosynthesis of gold nanoparticle (Ahmad et al. 2005). Authors showed that the shaking phase results in the formation of intracellular nanoparticles; however, an stationary phase (without shaking) also leads to the formation of extracellular nanoparticles (Ahmad et al. 2005). *Penicillium brevicompactum* was reported for the biosynthesis of silver nanoparticles using nitrate reductase enzyme (Hemath Naveen et al. 2010). An interesting study reported the biosynthesis of monodispersed silver nanoparticles using *Aspergillus fumigates* within 10 min (Bhainsa and D'souza 2006). This biosynthesis method for nanoparticles has been reported to be significantly rapid as compared to chemical and physical methods (Bhainsa and D'souza 2006). Based on abovementioned findings by various workers, it can be deduced clearly that biosynthesis of nanoparticles using fungal-based method is a rational, green, cost-effective, faster, and nontoxic approach. This is primarily due to the capability of fungi for reduction of the metal ions by an enzymatic process.

3.4 Introduction to Protein Aggregation

The specific functional and structural properties of protein aggregates play a key role in many routine physiological activities (Alsberg et al. 2006). However, the misfolding during protein assembly and aggregation could lead to several neurological disorders and diseases such as Huntington's, Alzheimer's, Parkinson's, and prion diseases to name a few (Lashuel et al. 2002). The protein aggregates defined as amyloids found in the patients with these disorders were characterized histologically more than 150 years ago (Aguzzi and O'Connor 2010).

3.4.1 Types of Protein Aggregates

Based on morphological analysis, protein aggregates can be categorized into two classes: ordered aggregates (amyloid) and disordered aggregates (amorphous) (Fink 1998). Amyloid fibrils are most commonly found extracellularly; however, there are various reports showing the presence of intracellular amyloid fibrils as well (Takahashi et al. 1989; Friedrich et al. 2010). Amyloids are known to have ordered structure with a high proportion of β -sheets (cross- β structure) and are known to demonstrate apple-green birefringence upon binding with dye Congo red (Fink 1998; Rambaran and Serpell 2008; Tycko 2011; Chiti and Dobson 2006). On the other hand, amorphous aggregates lack any ordered secondary structure (Fink 1998; Baneyx and Mujacic 2004; Villaverde and Carrio 2003).

3.4.2 Mechanism of Protein Aggregation

The mechanism of protein aggregation has been categorized into three different types such as nucleation dependent protein aggregation (seeded polymerization), templated assembly model, and nucleated conformational conversion mechanism (Philo and Arakawa 2009; Invernizzi et al. 2012; Idicula-Thomas and Balaji 2007; Gsponer and Vendruscolo 2006). Nucleation dependent polymerization consists of a rate limiting step, termed as lag phase, wherein oligomers form a critical nucleus and increase its size by the formation of the larger aggregates known as amyloids (Jarrett and Lansbury 1993; Eichner and Radford 2011). However, in template assembly model the protein aggregate functions as a template for straight addition of monomers (Griffith 1967). Nucleated conformational conversion mechanism consists of both the aforementioned mechanisms (Chatani and Yamamoto 2018). The latter aggregation pathway initially includes the formation of amorphous nuclei, which is followed by template assembly aggregation mechanism (Serio et al. 2000). The amyloid aggregates are known to follow the nucleation dependent polymerization pathway (Morris et al. 2009; Fink 1998; Eichner and Radford 2011).

3.4.3 *Therapeutic Intervention of Protein Aggregation Diseases*

Proteins tend to misfold and form aggregates under the specific stress conditions leading to the various human pathological disorders (Ross and Poirier 2004). Therefore, in order to control this, efforts are ongoing globally on controlling and/or reversing the formation of amyloid aggregates responsible for various neurodegenerative disorders (Sharma et al. 2012; Wang et al. 2013; Uversky 2007). Different approaches have been reported in the literature to deal with protein aggregation such as small peptides (Xiong et al. 2015), osmolytes (Macchi et al. 2012), antibiotics such as rifampicin (Tomiya et al. 1994), naturally derived polyphenols (Nedumpully-Govindan et al. 2016), and compounds based on amyloid binding dyes (Hasegawa et al. 2007). However, we will discuss about the nanoparticles as therapeutic agents for protein aggregation diseases.

3.4.4 *Nanoparticles as Therapeutic Agents*

Various studies have been reported on the effect of different nanoparticles on amyloid aggregation (Brambilla et al. 2011; Kogan et al. 2006; Araya et al. 2008). Gold and silver nanoparticles have been utilized in biomedical sciences (cancer treatment, controlled drug delivery, biomedical imaging, etc.) due to their apposite properties such as low toxicity, tunable stability, biocompatibility, small dimensions, and the possibility to interact with a variety of substances (Belanova et al. 2018). Recent studies have demonstrated that gold nanoparticles are capable of crossing the blood–brain barrier as well (Cabuzu et al. 2015; Cheng et al. 2014). Liao et al. have illustrated the effect of gold nanoparticles on amyloid aggregation (Liao et al. 2012). The authors showed that bare gold nanoparticles were able to abolish the formation of large fibrils and giving rise to fragmented fibrils and spherical oligomers (Liao et al. 2012). Authors further demonstrated that due to negative surface potential of gold nanoparticles, these act as nano-chaperones and further redirect and inhibit the amyloid aggregation. Recently a study demonstrated the biosynthesis of gold nanoparticles via extracellular mode using fungus *Fusarium oxysporum* (Mukherjee et al. 2002). The authors demonstrated that the extracellular synthesis of nanoparticles provided various advantages such as homogeneous catalysis when the nanoparticles were synthesized in solution form (Mukherjee et al. 2002). Xiong et al. have designed LVFFARK and LVFFARK-functionalized nanoparticles in order to prevent the amyloid- β protein aggregation (Xiong et al. 2015). A study reported that peptide-gold nanoparticles irradiated with microwave are capable of selective binding to β -amyloid and inhibiting the amyloidogenesis (Araya et al. 2008). Obulesu and Jhansilakshmi (2016) have synthesized redox nanoparticles such as nitroxide radical, 2,2,6,6 tetramethylpiperidiny-*N*-oxyl. They concluded

that piperine in association with redox nanoparticles confers improved prevention against Alzheimer's disease *in vitro*.

Another interesting study has attempted to interfere with amyloid- β aggregation growth and distantly re-dissolve these deposits via local heat dissipation of gold nanoparticles by selective binding to the aggregates (Kogan et al. 2006). Association with aggregates also allowed both, noninvasive exploration and dissolution of molecular aggregates. Therefore, based on abovementioned finding a conclusion can be drawn that a promising therapeutic approach for controlling the protein aggregation can be developed using different aspects of nanotechnology.

3.5 Future Prospect

Based on a recent study, it is estimated that Alzheimer's disease caused by amyloid plaques has affected about 44 million people worldwide (Alzheimer's Association 2015). This figure is expected to rise to 115 million by 2050 (Alzheimer's Association 2015). Presently, there is no competent therapy available for treating the patients with Alzheimer's disease. Moreover, another disadvantage of many of the available drug candidates is the incapability to cross the blood–brain barrier (Patel and Patel 2017). In that scenario, nanotechnology has emerged as a potential therapy in order to control the Alzheimer's disease due to the capability of various nanoparticles to cross the blood–brain barrier (Saraiva et al. 2016) and control the production and aggregation of amyloid plaques (Fig. 3.1). However, there are certain issues which have to be addressed to improve their efficacy. For example, the drug-loaded nanoparticles in comparison with the free drug, are currently limited quantitatively into the brain. Therefore, more focus should be paid on the development of systems transporting pharmacologically significant quantity of drugs into the brain. Moreover, a complete understanding of mechanisms of Alzheimer's disease will contribute towards the accurate application of targeted nanoparticles.

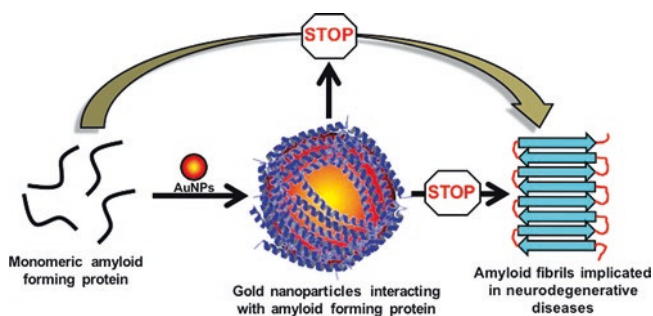


Fig. 3.1 Representative diagram showing the interaction of gold nanoparticles with the amyloid forming protein (e.g. amyloid β -peptide) in order to prevent its aggregation

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Chapter 4

Synthesis and Characterization of Selenium Nanoparticles Using Natural Resources and Its Applications



S. Rajeshkumar, P. Veena, and R. V. Santhiyaa

4.1 Introduction

Nanoparticles are the particles with nano size of less than 100 nm and one or more dimension. Nanoparticles have a higher surface area which gives larger target interaction. It has many important properties such as low melting point, catalytic activity, high photoconductivity, and high semiconductivity (Presentato et al. 2018; Prasad et al. 2016). This property of nanoparticles is used in the medical application (Palomo-Siguero et al. 2016). Nanoparticles are the very major part of nanotechnology playing an important role in the lot of applications related to biomedical engineering, chemical technology, environmental engineering, polymer technology, biotechnology, food science, agricultural development, etc. (Prasad et al. 2014, 2016, 2017). The nanoparticles used in various applications are gold, silver, silver oxide, copper, copper oxide, copper sulfide, zinc, zinc oxide, zinc sulfide, cadmium sulfide, titanium oxide, zirconium, cerium oxide, selenium, chitosan, cellulose, silica, iron, iron oxide, antimony trioxide, zirconium dioxide, platinum, and palladium (Mandal et al. 2006; Arvizo et al. 2010; Zhang et al. 2011; Dizaj et al. 2014; Rajeshkumar and Bharath 2017).

The different types of chemical and physical methods and materials are used in the synthesis of different nanoparticles using citrate, ammonia, sodium borohydride and radiation-chemical, microwave irradiation, electrochemical process, photochemical, ionic liquids, sonochemical and laser ablation (Dahl et al. 2007; Bhaduri et al. 2013). The biological synthesis of nanoparticles is developed vigorously

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nowadays (Fig. 4.1) with microorganisms such as bacteria like *Bacillus subtilis*, sulfate-reducing bacteria *Serratia marcescens*, *E. coli*, *B. licheniformis*, *Aeromonas* sp. *SH10*, *B. megatherium D01*, *Enterobacter cloacae*, *Klebsiella pneumoniae*, *Brevibacterium casei*, *Rhodobacter sphaeroides*, *Gluconacetobacter xylinus*, *Rhodopseudomonas palustris*, *Acetobacter xylinum*, *Klebsiella aerogenes*, marine bacteria *Enterococcus* sp., *Vibrio alginolyticus*, *S. oneidensis MR-1*, *Actinobacteria* sp., thermophilic bacteria *Thermoanaerobacter ethanolicus (TOR-39)*, *Sulfurospirillum barnesii*, *B. selenitireducens*, *Morganella* sp., *Thermophilic bacteria TOR-39*, *Geobacter metallireducens GS-15*, *P. boryanum UTEX 485*, *Lactobacillus* sp., *Sulfurospirillum barnesii* (Narayanan and Sakthivel 2010; Malarkodi et al. 2013a, b; Rajeshkumar et al. 2014b; Rajeshkumar 2016b). The different types of fungus are involved in the synthesis of various metal nanoparticles through intracellular and extracellular methods. Some of the fungus involved in the nanoparticles synthesis are *Penicillium fellutanum*, *Aspergillus flavus*, *Fusarium oxysporum*, *Colletotrichum* sp., *Trichothecium* sp., *Cladosporium cladosporioides*, *Penicillium brevicompactum*, *Phanerochaete chrysosporium*, *Trichoderma asperellum*, *Trichoderma viride*, *Phoma glomerata*, *Aspergillus niger*, *Coriolus versicolor*, *Mucor hiemalis*, and *Fusarium solani* (Lengke et al. 2011; Sharma et al. 2015; Aziz et al. 2016; Soumya et al. 2017).



Fig. 4.1 Green synthesis of nanoparticles

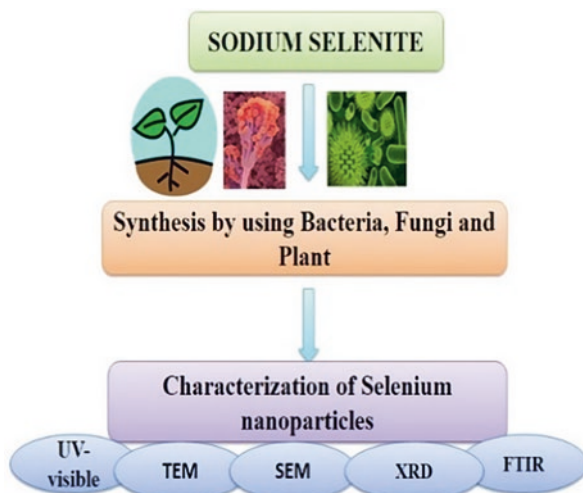
The marine macro algae such as *Sargassum wightii*, *Sargassum longifolium*, *Turbinaria conoides*, and *Padina tetraströmatica* are used in the synthesis of silver and gold nanoparticles synthesis and its applications on antibacterial, antifungal, and anticancer activities (Rajeshkumar et al. 2012, 2013a, b, 2014a, Sangeetha et al. 2017a, b). Apart from this some other natural resources like viruses tobacco mosaic virus (TMV) used in the synthesis of SiO₂, Fe₂O₃, CdS, and PbS, and M13 bacteriophage used in the semiconductor nanoparticles synthesis. The yeast *Candida glabrata*, *Schizosaccharomyces cerevisiae*, *Yarrowia lipolytica*, *Torulopsis* sp., *Pichia jadinii*, and *S. pombe* also involved in the biosynthesis of many metals and metal oxide nanoparticles (Mandal et al. 2006; Narayanan and Sakthivel 2010; Thakkar et al. 2010; Lengke et al. 2011; Moses 2014).

Finally the plants, one of the major resources used in the green synthesis of different types of nanoparticles and a lot of phytochemicals present in the plant responsible for the nanoparticles production. Some important plants involved in the green synthesis of nanoparticles are *Pongamia pinnata*, *Passiflora* sp., *Coleus aromaticus*, *Andrographis paniculata*, *Solanum Xanthocarpum*, *Capsicum annum*, *Coriandrum Sativum*, *Euphorbia hirta*, *Gliricidia sepium*, *Ficus carica*, *Lippia citriodora*, *Paederia foetida*, *Rosa rugosa*, *Catharanthus roseus*, *Elaeagnus Indica*, *Arbutus unedo*, *Allium cepa*, *Fissidens minutes*, *Elaeagnus latifolia*, *Ocimum bacillicum*, *Anogeissus latifolia*, and *Vitis vinifera* (Vanaja and Annadurai 2012; Gnanajobitha et al. 2013; Vanaja et al. 2013, 2014; Prasad 2014; Paulkumar et al. 2014; Rajeshkumar 2016a; Rajeshkumar and Bharath 2017). The biomolecules present in the bacteria, fungus, algae, yeast, plant, and virus are major agents responsible for the synthesis of metal oxide, metal and metal sulfide nanoparticles synthesis and characters. The Fourier transform infrared spectroscopy is the major technique used in the identification of functional group involved in the synthesis of nanoparticles. Some of the biomolecules involved in the green synthesis of nanoparticles are proteins, carbohydrates, sulfated polysaccharides, nitrate reductases, carotenoids and NADPH-dependent enzymes 90-kDa protein, 66- and 10-kDa protein, membrane-bound quinine or membrane-bound/cytosolic pH-dependent oxidoreductase, glutamate and aspartate on the surface, peptidoglycan reducing sugars, α -NADPH-dependent sulfite reductase (35.6 kDa), and phytochelatin (Narayanan and Sakthivel 2010; Paulkumar et al. 2013, 2014; Prasad et al. 2016). A possible green synthesis of various nanoparticles using plant and/or plants' part has been illustrated in Fig. 4.2.

4.2 Selenium Nanoparticles

Selenium is one of the important trace elements which is required up to 40–300 μ g for human body every day. It helps in regulating the function of the human body. It helps in protecting cardiovascular health, regulating thyroid hormones and immune response, and preventing progression of cancer (Gautam et al. 2017). The only small amount is required for maintaining the function, and a large amount of

Fig. 4.2 Green synthesis of selenium nanoparticles and its characterization



selenium may be harmful to the human body (Srivastava and Mukhopadhyay 2015a). Selenium has codons in mRNA which form seleno-cysteine by inserting as selenoprotein. Thioredoxin reductase and glutathione peroxidase are the enzymes comprising selenoprotein that function as antioxidant and detoxificant (Srivastava and Mukhopadhyay 2015b). Vitamins, ATP, and other capping agent stabilize and control the size, and they also increase the circulation and uptake of selenium nanoparticles (Zhu et al. 2017). Selenium also acts as an alternate for gold in alcohol beverage industry (Kalishwaralal et al. 2015). Selenium is less toxicity and high activity of selenium nanoparticles are used in many medical applications such as anticancer (Huang et al. 2013; Ramamurthy et al. 2013), antimicrobial (Bartůňek et al. 2015), drug delivery. The human body is able to degrade selenium nanoparticles naturally; the residues of the selenium nanoparticles act as the selenium nutrient source and are not toxic to the human body. High surface area and the low particle size of selenium nanoparticles enhance the biological activity. Selenium nanoparticles actively work against the antibiotic-resistant bacteria which has been increased recently (Bartůňek et al. 2015). The average size of the selenium nanoparticle is 80 nm and the property and activity of the selenium nanoparticles depend on the size, shape, and the biomolecule's nature (Husen and Siddiqi 2014).

Selenium nanoparticles can be synthesized by various methods. Usually, SeNPs is synthesized by the biological method and chemical method. Biological method of synthesis of selenium nanoparticle is by using living organisms such as bacteria, yeast, fungi, and plants (Husen and Siddiqi 2014; Ezhuthupurakkal et al. 2017; Hamza et al. 2017). Selenium nanoparticles synthesized using biological method have many applications such as antibacterial, antifungal, and also against pathogenic yeast (Dutta et al. 2014; Fernández-Llamosas et al. 2016). Chemical method of synthesis of selenium nanoparticles is by using chemicals as reducing agent for reducing selenite to selenium nanoparticles (Panahi-Kalamuei

et al. 2014). Many other methods are also followed to synthesize selenium nanoparticles such as chemical vapor deposition, template free, template-assisted and electrodeposition (Chen et al. 2011).

4.3 Chemical Synthesis of Selenium Nanoparticles

Biopolymers such as gum acacia, glutathione, sodium alginate, and carboxymethyl cellulose are used for the synthesis of selenium nanoparticles (Tayebee et al. 2005). Several studies were carried out with the synthesis and application of the selenium nanoparticles. Different sizes of selenium nanoparticles are synthesized by facile reduction method by using ascorbic acid as reducing agent and to control the reaction kinetics polysorbate 20 surfactant is used. TEM is used to analyze the size and quality of the selenium nanoparticles. AAS is used to assess the presence of selenium. XRD is used to measure the structure of the nanoparticles. Three bacterial strains are used to test the antibacterial property of the synthesized nanoparticles. Selenium nanoparticles showed activity against common gram-positive bacteria *Staphylococcus epidermidis* and *Staphylococcus aureus* (Bartůněk et al. 2015). Selenium plays an important role in human health. The cells are protected by selenium from free radical. Bovine serum albumin and keratin are used to synthesize two different sized selenium nanoparticles. The characteristics of synthesized selenium nanoparticles are analyzed using SEM, XRD, and EDX. In vivo and in vitro antioxidative property of the selenium nanoparticles and sodium selenite is studied. The results show that the selenium nanoparticles can be effectively used in the alcoholic beverage industry as an additive (Kalishwaralal et al. 2015) by using beta-lactoglobulin as a stabilizer and ascorbic acid as reducing agent. TEM, dynamic light scattering (DLS), ultraviolet visible spectrophotometry, and FTIR are used to analyze the size, shape, structure, morphology, biological activity, and stability. Bls- SeNPs is highly stable in higher and lower pH. The synthesized nanoparticles are spherical in shape and the toxicity of the selenium nanoparticles is lower than that of selenite (Zhang et al. 2017). Lentinan is naturally occurring β -glucan which is used as stabilizing selenium nanoparticles. Transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-Ray (EDX), dynamic light scattering (DLS), and ultraviolet visible spectrophotometry are used to analyze the characteristics of the selenium nanoparticles. By controlling the concentration of the sodium selenite and the reducing agent, different size of the selenium nanoparticles are obtained. The anticancer activity of the selenium nanoparticles is based on the distribution of size (Jia et al. 2015). The shape of the selenium nanoparticles is controlled by designing the chemical structure of the stabilizing agent by a self-assembly process. Three hundred nanometer, the cubic structure of the selenium nanoparticles are synthesized using the folic acid-gallic acid-*N, N, N*-trimethyl chitosan as a stabilizing agent. Two hundred nanometer, spherical shaped particles are produced using unmodified chitosan. Better uptake of breast cancer cells and lesser toxicity towards noncancer cells are achieved by using cubic selenium nanoparticles (Luesakul et al. 2016).

4.4 Biological Synthesis of Selenium Nanoparticles

Synthesis of selenium nanoparticles by using bacterial biomass has gained huge interest due to its low cost, high effect, and environment-friendly nature. Several types of bacteria, yeast, fungi, and parts of plants are used based on its tolerance to selenite in order to convert it into selenium nanoparticles. Actinomycete, *Rhodococcus aetherivorans* BCP1 is anaerobic bacterium which is used to convert selenite into selenium nanoparticles. The strain has 500 mM of MHC and has high tolerance towards selenite. Two states of cells are used in bioconversion, conditioned and unconditioned. Bioconversion process is more effective in conditioned cells (Presentato et al. 2018). Fish gills were used to synthesize the selenium nanoparticles and used in thermal tolerance enhancement of *Pangasius hypophthalmus* high temperature and lead concentration (Kumar et al. 2017). A fast-growing bacterium *Vibrio natriegens* is used in the bioconversion of selenite into selenium nanoparticles. *Vibrio natriegens* is easily engineered with the gene of interest and can be grown with any carbon source. *Vibrio natriegens* has a high tolerance to selenite at an extreme concentration of 100 mM and effective growth is observed in 15 mM. X-ray spectroscopy and an electron microscope are used to analyze the characteristics of synthesized selenium nanoparticles and the growth of *Vibrio natriegens* on selenite. Culture is grown in LB media; spherical shaped selenium nanoparticles with 100–400 nm size are synthesized. Reduction of selenium is seen in the exponential growth phase of the cell and the synthesis of selenium nanoparticles is seen in cell lysis. *Vibrio natriegens* is used to enhance the speed of the production of selenium nanoparticles (Fernández-Llamosas et al. 2017). Development of an appropriate method for synthesis and retrieval of the nanoparticle is necessary. Selenium nanoparticles are synthesized using *Klebsiella pneumonia* strain from selenium chloride. Culture broth is sterilized at 121 °C for 20 min at 17 psi. Synthesized nanoparticles are 100–550 nm. Wet heat sterilization is carried out since no chemical changes are obtained (Fesharaki et al. 2010). Proteins also play an important role in the synthesis of the selenium nanoparticles. It involves in the production of selenium nanoparticles by reducing selenium oxyanions. Proteins involve in reduction of selenite to selenium and also they are involved in the stabilization of the selenium nanoparticles. The structure of the biosynthesized nanoparticles is different with the chemically synthesized nanoparticles. Their structure and characteristics are also analyzed (Tugarova and Kamnev 2017). Table 4.1 depicts the green synthesis of selenium nanoparticles along with their shapes and sizes.

Selenium nanoparticles synthesized using actinobacteria possess several other properties such as antioxidant, antiviral, and anticancer. *Streptomyces minutiscleroticus* M10A62 are able to synthesize selenium nanoparticles extracellularly. The different types of analysis such as XRD, FTIR, HR-TEM, and UV visible spectroscopy are carried out to study the characteristics of the selenium nanoparticles. The nanoparticles synthesized are of 100–250 nm with identical sphere structure. The selenium NPs synthesized from actinobacteria has activity against dengue virus (Ramya et al. 2015). *Enterococcus faecalis* are able to synthesize selenium NPs from

Table 4.1 Green synthesis of selenium nanoparticles

Source	Scientific name	UV-visible (nm)	FTIR	Size (in nm)	Shape	References
Bacteria	<i>Streptomyces minutiscleroticus</i>	510	FTIR shows that the protein secondary structure binds with the NPs	10–250	Spherical	Ramya et al. (2015)
Bacteria	<i>Enterococcus faecalis</i>	200–1000	–	29–195	Spherical	Shoeibi and Mashreghi (2017)
Bacteria	<i>Azospirillum brasilense</i>		FTIR shows that the surface of selenium NPs is capped by the polysaccharides and proteins of biomacromolecules	50–100	Nanosphere	Kamnev et al. (2017)
Bacteria	<i>Zooglea ramigera</i>	330	–	30–150	Spherical	Srivastava and Mukhopadhyay (2013)
Bacteria	<i>Alcaligenes</i> sp.	300–800	–	90–120	Rod-like structure	Mesbahi-Nowrouzi and Mollania (2018)
Bacteria	<i>Idiomarina</i> sp. PR58-8	320	–	150–350	Spherical	Srivastava and Kowshik (2016)
Bacteria	<i>Pseudomonas aeruginosa</i>	300–900	FTIR peaks show that the bacterial protein involves in the synthesis and stabilization of NPs	47–165	Spherical	Kora and Rastogi (2016)
Bacteria	<i>Stenotrophomonas maltophilia</i>		Carbohydrates, proteins, and lipids act as the capping agent	160–250	Spherical	Lampis et al. (2017)
Bacteria	<i>Azospirillum thiophilum</i>		FTIR shows that the surface of selenium NPs is capped by the polysaccharides and proteins of biomacromolecules	160–250	Nanosphere shape	Tugarova et al. (2018)
Proteobacteria	<i>Burkholderia fungorum</i>		–	170–200	Spherical	Khoei et al. (2017)

(continued)

Table 4.1 (continued)

Source	Scientific name	UV-visible (nm)	FTIR	Size (in nm)	Shape	References
Protozoa	<i>Tetrahymena thermophila</i> <i>SB210Yin</i>	240–600	–	50–500	Amorphous sphere	Cui et al. (2016)
Yeast	<i>Yarrowia lipolytica</i>	220	Presence of the amine and carboxylic group in nanoparticle synthesis			Hamza et al. (2017)
Yeast	<i>Pichia pastoris</i>		–	180	Spherical	Elahian et al. (2017)
Fungi	<i>Cordyceps sinensis</i>	200–800	The result shows that surface atom of SeNPs and OH group of EPS has strong bonding	80–125	Homogenous sphere	Xiao et al. (2017)
Plant	<i>Azadirachta indica</i> leaf	600	The FTIR result shows that the selenium nanoparticles and the biomolecule of the plant leaf have the physical interaction	35	Spherical	Tareq et al. (2018)
Plant	<i>Allium sativum</i>	200–800	Peaks in FTIR confirm that the formation of SeNPs is due to the organic acid, polymeric agent of <i>Allium sativum</i> and they also act as the stabilizing agent	205	Crystalline sphere	Ezhuathupurakkal et al. (2017), Satgurunathan et al. (2017)
Plant	Lemon leaf	395	Hydroxyl, amine, carboxyl are involved in SeNPs synthesis	60–80	Sphere	Prasad et al. (2013)
Plant	Fenugreek seed	200–400	FTIR shows that the selenium acid reduction is due to the bond stretching and bending of functional group	50–150	Oval	Ramamurthy et al. (2013)
Plant	<i>Vitis vinifera</i>		The result shows that the selenium nanoparticles are synthesized using the reducing agent present in the <i>V. vinifera</i> .	3–18	Sphere	Husen and Siddiqi (2014)
Plant	<i>Bougainvillea spectabilis</i> wildflower	590	Flavonoids present in the <i>B. spectabilis</i> act as the reducing agent in the synthesis of SeNPs	25	Hollow crystals	Ganesan (2015)

Source	Scientific name	UV-visible (nm)	FTIR	Size (in nm)	Shape	References
Plant	<i>Catharanthus roseus</i>	325	Reduction of sodium selenite is due to the vibration by stretching of ketone	17–34	Spherical	Deepa and Ganesan (2015)
Plant	<i>Peltophorum pterocarpum</i>	325	–	21–42	Spherical	Deepa and Ganesan (2015)
Plant	<i>Diospyros Montana</i>	270–350	Alkaloids, steroids, and flavonoids from leaf act as the capping agent	4–16	Spherical	Kokila et al. (2017)

sodium selenite. The characteristics of the NPs are analyzed using TEM and UV-spectroscopy. TEM reveals that the size of the NPs is 29–195 nm and is spherical in shape (Shoebibi and Mashreghi 2017). *Idiomarina* sp. PR58-8 is a bacteria used in the process of reduction of sodium selenite to selenium nanoparticles. The nanoparticles are 150–350 nm in size and spherical in shape. The synthesized nanoparticles are highly anti-neoplastic (Srivastava and Kowshik 2016). In vivo synthesis of selenium nanoparticles by protozoa is environment-friendly without complicated devices. Several other genes are also regulated with the nanoparticles producing group. The synthesized nanoparticles are spherical in shape with diameter of 50–500 nm (Cui et al. 2016). A biomass of rhizobacterium azospirillum brasiliense is used to synthesize selenium nanoparticles by selenite reduction. FTIR and TEM are used to analyze the structure and morphology which reveals that the nanoparticles are homogenous with average diameter 50–200 nm (Kamnev et al. 2017). The bacterial protein of *Zooglea ramigera* is responsible for the reduction of selenium nanoparticles. The prepared nanoparticles are hexagonal phase nanocrystals. XRD, TEM, SEM, SAED, and DLS are carried out to test the characteristics of the nanoparticles which reveals that the SeNPs is 30–150 nm and spherical in shape (Srivastava and Mukhopadhyay 2013). Gram-negative bacteria *Pseudomonas aeruginosa* is used in the reduction of selenite to selenium nanoparticle. Presence of selenium nanoparticles is confirmed by UV-spectra peaks and the color change to red in broth.

Cordyceps sinensis is a fungus that is used to synthesize EPS conjugated selenium nanoparticles. Characteristics are analyzed and the results reveal that the size is uniform and the shape is a 80–125 nm homogenous sphere (Xiao et al. 2017). *Azadirachta indica* leaf is used in the reduction of selenium ion to selenium nanoparticle. By conducting different analysis it is found that the selenium nanoparticles are spherical in shape and have average size of 35 nm. The synthesized nanoparticles are antibacterial and antioxidant (Tareq et al. 2018). Eco-friendly preparation of selenium nanoparticles is done by using an aqueous extract of *Allium sativum* which has good interaction with the DNA. This property is used in chemotherapy for DNA targeted (Ezhuthupurakkal et al. 2017). Selenium nanoparticles synthesized using lemon leaf extract are used to treat the DNA damage caused by UV exposure (Prasad et al. 2013). Fenugreek seed extract is also used for reduction of the selenious acid to selenite nanoparticles in an eco-friendly process. The synthesized nanoparticles are loaded with doxorubicin which acts as an anticancer agent. Flower of *Bougainvillea spectabilis* will be used for reducing sodium selenite to selenium nanoparticles. The synthesis is easy, cost-effective, and fast (Ganesan 2015). Using the aqueous extract of the Diospyros Montana leaf, selenium nanoparticles are synthesized by the eco-friendly process. The synthesis is a simple precipitation process and different analysis is made for characterization of the synthesized nanoparticles (Kokila et al. 2017). Detailed applications of selenium nanoparticles have been summarized in Table 4.2.

Yarrowia lipolytica is marine yeast that shows tolerance for the sodium selenite and is able to form selenium nanoparticles. *Artemia salina* is fed with the selenium nanoparticles rich biomass and the size of the larvae is found to be larger (Hamza et al. 2017). Applications of selenium nanoparticles in various fields have been illustrated in Fig. 4.3.

Table 4.2 Applications of selenium nanoparticles

Field	Application	Remarks	References
Antibacterial	Selenium NPs act against <i>Staphylococcus aureus</i> which is used in catheterization and prosthesis	8 mm zone is obtained in disc diffusion test	Shoeibi and Mashreghi (2017), Huang et al. (2016)
	Multidrug-resistant superbugs	Quercetin and acetylcholine decorated on the surfaces of the Se NPs act as antibacterial against MRSA	
Drug delivery	HepG2 hepatocellular carcinoma, breast adenocarcinoma cells are tested with doxorubicin	Cell apoptosis is promoted by activating p53 pathway	Huang et al. (2013)
	Human breast carcinoma cells, murine colon carcinoma cells are inhibited by epirubicin	Human breast carcinoma cells, murine colon carcinoma cells are inhibited by epirubicin	Jalalian et al. (2018)
Cancer	Therapeutic agent	Several biomacromolecules, polymers, and metals are conjugated with selenium NPs to achieve maximum efficacy for human cancer	Fernandes and Gandin (2015)
Dye degradation	Degradation of model dye trypan blue	ROS generated by the selenium doped zinc nanoparticles are efficient in degrading trypan blue	Dutta et al. (2014)
Inhibits biofilm	Staphylococcus aureus biofilm formation is inhibited	SeNPs synthesized using Bacillus licheniform is used for inhibiting the growth of Staphylococcus aureus adherence on surfaces	Sonkusre and Singh Cameotra (2015)
Cancer	Chemoradiation for cervical cancer cells, mouse embryonic fibroblast	Selenium NPs with PEG surface decorated possess X-ray responsive property and act as a therapeutic agent for cancer	Yu et al. (2016)
Anti-leishmaniasis	Selenium nanoparticles and selenium dioxide are tested against <i>Leishmania infantum</i>	Selenium nanoparticles are more efficient than selenium dioxide	Soflaei et al. (2014)

Selenium nanoparticles synthesized from *Enterococcus faecalis* are active against *Staphylococcus aureus*. Antibacterial test for selenium nanoparticles against gram-positive bacteria *Bacillus subtilis*, *Staphylococcus aureus* and gram-negative *Pseudomonas aeruginosa* and *Escherichia coli* is done by disc diffusion method. The result shows that selenium nanoparticles are active against *Staphylococcus aureus* with 8 mm zone (Shoeibi and Mashreghi 2017). Multidrug-resistant superbugs are also a great threat to the world. To overcome this selenium nanoparticle is decorated with quercetin and acetylcholine on the surface which permanently damage the cell membrane of methicillin-resistant *Staphylococcus aureus* (Huang et al. 2016).

Fig. 4.3 Applications of selenium nanoparticles in various fields



Selenium nanoparticles have great attention towards cancer therapy. Nanoparticles are widely used for a selected target which reduces the effect on normal cells. Nanoparticles based drug delivery is widely due to its major advantages. Transferrin-conjugated selenium nanoparticles is loaded with cancer drug doxorubicin. By activating p53 and MAPKs pathways, transferrin-conjugated SeNPs mediate cell apoptosis. This design of drug delivery decreases the side effects and increases the efficiency (Huang et al. 2013). Dye degradation is enhanced by the oxidation process which is carried out by the selenium doped zinc nanoparticle for degrading trypan blue dye. The degradation is carried out by selenium doped zinc nanoparticle by ROS oxidative system (Dutta et al. 2014). Selenium nanoparticles synthesized using *Bacillus licheniformis* are used for inhibiting the biofilm formation of *Staphylococcus aureus* on surfaces such as glass, catheter, and polystyrene which can be used to prevent the formation of biofilm on medical devices (Sonkusre and Singh Cameotra 2015). Chemoresistant and radioresistant cancer cells are treated using chemoradiation. Selenium nanoparticles decorated with PEG have an X-ray responsive property and the growth of cancer is inhibited by cell apoptosis (Yu et al. 2016).

4.5 Conclusion

Selenium nanoparticles are synthesized using living organisms and physical/chemical method. SeNPs prepared using bacteria have high effect against pathogenic bacteria and yeast. Selenium nanoparticles show less toxicity towards normal cells and more toxic to cancer cells. This property can be used in drug delivery and for cancer therapy. Selenium nanoparticles are degraded by the human body naturally and the selenium acts as a source of nutrients for the function of the human and animal

body. Selenium nanoparticles synthesized using several methods possess many important properties which can be used in different applications such as drug delivery, cancer therapy, and dye degradation. This property enhances the use of selenium nanoparticles in the medical and biological field.

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Chapter 5

Nanofabrication by Cryptogams: Exploring the Unexplored



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5.1 Introduction

The canvas of nanotechnology recounts diverse fascinating endeavours to control, understand, and manipulate matters at infinitesimal scale. This rapidly emerging and fascinating technology, that deals with nanometre (10^{-9}) sized entities, as a breakthrough among the existent technologies, promises to unravel the nanoscale processes for novel applications. Cells, which is considered as the basic unit of all living organisms, are usually the size of $10\ \mu\text{m}$ while the cell organelles although smaller yet lies in the micron size. The size of proteins, which is roughly around $5\ \text{nm}$, is equivalent to the size of smallest manmade nanoparticles (Taton 2002). This gives an idea as to how small 'nano' is and nanomaterials with dimension lying amidst $1\text{--}100\ \text{nm}$ are blessed with amazing properties as compared to its bulk counterpart. Novel properties of materials at the nanoscale may be attributed to its altered physicochemical properties and surface to volume ratio (Suman et al. 2010). At nanoscale, the optical (Parak et al. 2003), physical, and magnetic (Pankhurst et al. 2003) properties are amended, and this leads to outspread applications of these entities in variegated sectors, medical sector being one of them.

With the increasing implementation of nanomaterials in diversified sectors the urge for its legitimate fabrication route is of prime concern. Nanofabrication is achieved by two types of amenable approaches, namely top down approach and bottom up approach as depicted in Fig. 5.1. In top down approach, a bulk piece of material is engraved to nano size through processes like mechanical grinding, ball milling, thermal evaporation, explosion process, and different kinds of lithographic cutting

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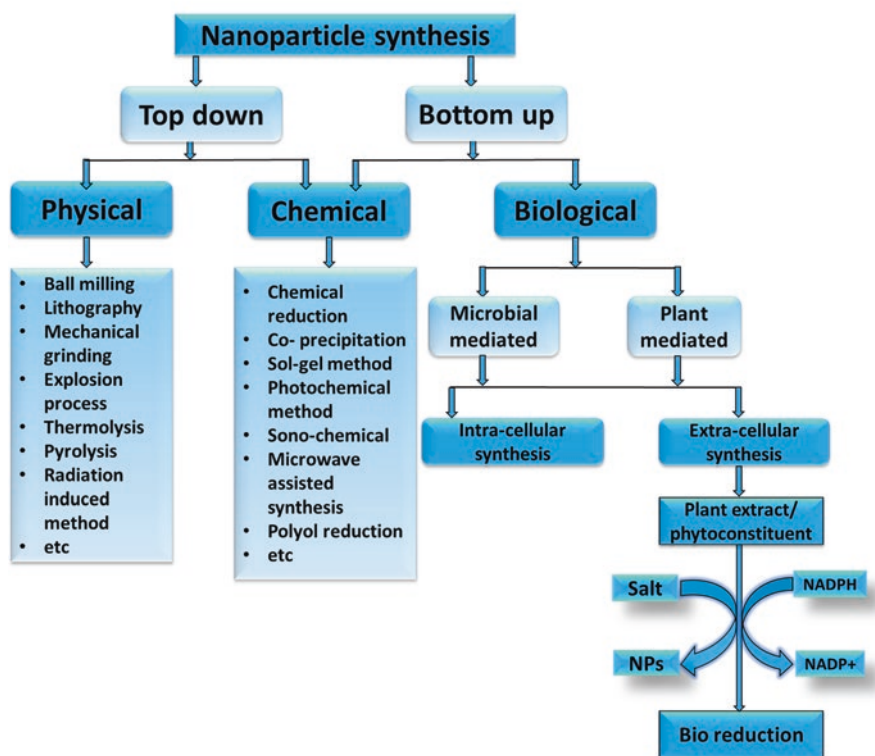


Fig. 5.1 The amenable approaches for nanofabrication

techniques like photo ion beam or X-ray lithography cutting (Li et al. 1999a, b). Top down approaches lead to some imperfections on the surface. This is a major disadvantage of this method because the surface structure plays an important role in physical properties of nanoparticles (Thakkar et al. 2010). Bottom up approaches are basically driven by self-arrangement of atoms to fabricate the nanomaterial through atom-by-atom and molecule-by-molecule interaction. The bottom up synthesis generally depends on chemical and biological methods. Chemical routes involve condition such as use of strong chemicals, reducing agents, capping agents, high temperature, and pressure, with protective agents (e.g. sodium borohydride, sodium citrate, alcohol). These organic solvents along with the reducing and capping agents are toxic, flammable, and their release in environment causes environmental hazards. Occurrence of these harsh chemicals limits the chemical route of fabrication and the further applicability of nanomaterials in areas like medical sector. In order to have biological and environmental safety in nanofabrication, the biological fabrication route applicability was considered. The living world is controlled by most efficient and best eco-friendly nanoscale processes, and this was a clue to the quest for an eco-friendly fabrication route. In contrast to physical and chemical methods,

in this route natural biological agents are used for hydrolysing the metals. It is a simple, nontoxic, less labour intensive, low cost, environment-friendly greener approach of nanofabrication with no disposal issues. The biological agents used for fabrication are microorganisms (bacteria, fungi, actinomycetes), yeast, algae, and plants (bryophytes, pteridophytes, angiosperm, gymnosperm). Synthesis based on microorganisms has been commonly reported (Sastry et al. 2003; Gericke and Pinches, 2006; Mohanpuria et al. 2008; Korbekandi et al. 2009; Li et al. 2010; Sanghi and Verma, 2010; Kaler et al. 2011; Luangpipat et al. 2011; Dhillon and Mukhopadhyay 2015; Prasad et al. 2016). Synthesis from microbes can be scaled up in the lab, but as far as production is concerned, it is more expensive than plant extracts. The plant-mediated nanoparticles remain stable in nature for long time, and the rate of synthesis is also faster as compared to the microbes. Synthesis from plant extracts is a one-step, efficient, inexpensive, and environmentally safe method for producing nanoparticles with specified properties. The plant biomolecules besides being involved in bio-reduction also helps in stabilizing the nanoparticles and enhancing its properties. Therefore, plant-mediated nanoparticle fabrication is significant in all prospects (Park et al. 2011; Prasad 2014). The plant diversity is rich and bestowed with members starting from microscopic algae to giant trees. Each member has its important role in maintaining the ecosystem and all are rich in diverse metabolites, capable of nano-transformation. Numerous nanoparticles have been synthesized and reported from phanerogams (angiosperm and gymnosperm) (Prathna et al. 2010), but fewer attempts have made in this direction with lower cryptogamic plants. These cryptogams are rich sources of diverse metabolites and have been used as ethnomedicine since ages. The success story of initial attempts of nanofabrication through these cryptogams has proved them to be strong contenders in the plant world. This chapter attempts to explore these salient members as tools for nanofabrication. It presents an overview about cryptogams, its phylogeny, and role in plant diversity along with its ethnomedicine properties. The focal point of this chapter will be the nanofabrication via the cryptogams (bryophytes and pteridophytes), summarizing all the reports till date along with the characterization tools used and deciphering the fundamental science behind the fabrication. Special attention will be given to the fabricated nanoparticles biomedical applications and effect on human health.

5.2 Cryptogams: Salient Component of Plant Diversity

Cryptogams are integral part of plant diversity and ecosystem, playing important role in ecological balance. These are non-seed-bearing plants reproducing by spores and are divided into four orders, namely fungi, algae, mosses (bryophytes), and ferns (pteridophytes) (Smith, 2014). Nowadays, fungi are specified in separate kingdom, more closely to animals than plants and algae (thallophyte). The order algae are an enlarged group with numerous members and in nanotechnological perspective many members have been exploited for nanofabrication. This chapter tends to

explore the other two members of the cryptogam family, namely bryophytes and pteridophytes wherein the penetration of nanotechnology is meagre. In the compass of bryophytes and pteridophytes, there are only few reports of nanofabrication through them. Before getting into the nanofabrication sphere, there is a need to have an overview of distribution and appliance of these members for better understanding as to why they are important as fabricators.

Bryophytes taxonomically exists between pteridophytes and algae, there are approx. 24,000 species in the world. These are cellular (non-vascular) simply organized plant body with a single spore-forming organ. Their species are classified into three main groups: Firstly, Anthocerotophyta (hornworts), which has approximately 300 species, secondly Marchantiophyta (liverworts), which has approximately 6000 species and lastly, Bryophyta (mosses), which has approximately 14,000 species. They have the ability to grow on bare soil and cracks of rocks because they do not depend on roots for their nutrition from soil, but a thin layer of water is mandatory on the surface of the plant for reproduction and survival (Shaw et al. 2011). Therefore, they are found in ranges from chilly to desert, sea to alpine, and dry to wet rainforest (Everet and Susan 2013). Pteridophytes are richly found in several different habitats of the world. In Carboniferous period, they were leading, hence named as 'Age of Ferns'. Most of the carboniferous ferns are extinct, but some of these ferns have evolved. Around 12,000 species of pteridophytes are existing in the world (Antony et al. 2000). They are vascular plants, with xylem and phloem for nutrition, water and gas movements (Schuettpelez et al. 2016). These ferns are mainly found in humid, moist, well-drained sites, and crack of rock walls for growth. Such wide distribution in almost all the habitats displays that these cryptogams are allotted with rich phyto-constituents that give them the ability to restrain the environmental challenges.

5.2.1 Appliance of Cryptogams

The bryophytes and pteridophytes are bestowed with many rich and treasured phytochemicals that make them valuable and accounts for their diverse applications. Bryophytes besides being used as bioindicators for the presence of heavy metals in soil and air pollution are also used to improve soil conditions, by water retention in air space within soil (Kumar et al. 1999). Some bryophytes have been used as natural pesticides, biochemicals produced by bryophytes act as antifeedants, for example: the liverwort, *Plagiochila* are poisonous to mice (Glime 2007). *Pythium sphagnum* inhibits growth of fungus; this antibiotic property of bryophytes makes them a valuable packaging material and surgical dressing tool (Glime 2007). Although enriched with remarkable quality, bryophytes largely remain unexplored and untouched in many aspects, nanofabrication being one of them. Pharmacological analysis of bryophytes as studied by many researchers revealed out unique and active compounds that have the potential of therapeutic applications. At present,

approximately 400 new compounds have been isolated and categorized for their biochemical and antimicrobial properties. Mostly, bryophytes can't be damaged by insects, and other small animals, because of fragrant odours and an intense bitter taste. They are rarely infected by microorganisms because of the presence of metabolites. These biologically active compounds enhance their medicinal importance worldwide (Ilhan et al. 2006). Many bryophytes are being used in medicinal purposes like burns, wounds, and bruises (Cramer et al. 1999). Active biological substances found in bryophytes, with respect to their bio-chemistry, pharmacology, and applications are used in cosmetics and medicinal drugs. Most of the bryophytes are rich in alkaloids (lycopodine, clavatine, nicotine), aromatic compounds (isocoumarins, cinnamates, bibenzyls, bis-bibenzyls, benzoates, naphthalenes, phthalides), flavonoids (apiginine and triterpene), and oil bodies (acetogenins). The presence of these compounds enhances their biological activities (Asakawa et al. 1995, Asakawa 2001) and also suggests their appliance as nanofabricators. The di-terpenoids and aromatic compounds isolated from the bryophytes (Lohlau et al. 2000) are used as antibacterial agent (Banerjee 2001; Scher et al. 2004; Sabovljevic et al. 2006; Mathur et al. 2007; Dulger et al. 2009), antifungal agent (Alam et al. 2011, 2012), anti-HIV, cytotoxic agent, DNA polymerase inhibitor (Rhoades 1999; Asakawa 2001), antioxidant, and antitumor agents (Vats et al. 2012; Sathish et al. 2016). The wide distribution of bryophytes in all habitats and the presence of abundant ethno therapeutic compounds make them a competent candidate for nanofabrication.

There are around 1250 species of pteridophytes found in India; out of these approx. 173 species have been found to be used as medicine, bio-fertilizers, green-manure, food, and flavour and dye (Manickam and Irudayaraj 1992). The presence of essential biological compounds enhances its popularity among plants. The presence of phenolic group attributes effective antioxidants property; flavonoids help to decrease the risk of cancer, cardiovascular disease, and other age-related diseases. Ancient people were using these ferns for ethno-medicinal purposes (Britto et al. 2012). These plants have been effectively used in homeopathic, ayurvedic, and unani system of medicines (Khare 2007). The pteridophytes have been efficiently used as antimicrobial (Dalli et al. 2007; Parihar et al. 2010) as well as an antioxidant agents (Lai and Lim 2011). Dihydrochalcone isolated from *Pityrogramma calomelanos* is a potential antibiotic and anticancer chemotherapeutic agent (Sukumaran and Kuttan 1991). The tribal groups have been using rhizomes, stem, fronds, pinnae, and spores in various ways for the treatment of various ailments (Kumari et al. 2011). The rhizome of fern is a pouch for storage of food as well as variety of secondary metabolites. Although pteridophytes are store house of such important bioactive compounds, sufficient attention has not been paid towards their valuable aspects, especially the phytochemical constituent usage. Pteridophytes belonging to the group of lower plants are rich in metabolites, but because of ignorance it remains unattended and their useful aspects are largely unexplored. Biochemical constituent of these pteridophytes makes it a suitable candidate for the fabrication of nanomaterials.

5.2.2 *Phylogeny of Cryptogams*

In the plant kingdom, plants are classified on the basis of geographies, their similarities and dissimilarities. In 1883, Eichler classified whole plant domain, known as the traditional phylogenetic system. Eichler divided plant kingdom into two subkingdoms (cryptogams and phanerogams). The cryptogams were further subdivided into three divisions: thallophyta, bryophyta, and pteridophyta. Bryophytes parted into three classes: Marchantiophyta, Anthocerotophyta, and Bryophyta. Pteridophytes parted into two classes: lycopodiopsida and polypodiopsida. The phylogeny of cryptogams as represented in Fig. 5.2, provides an ecological relationship, showing similarities and dissimilarities among its members. This knowledge may help in deciphering a common probable mechanistic aspect of nano-transformation by these members.

5.3 *Nanofabrication Using Cryptogams*

In several papers, researchers have often reported synthesis of nanoparticles from phanerogams (angiosperms and gymnosperms). However, very slight work has been done in the lower groups like bryophytes and pteridophytes (cryptogams), primitive plants with highest assemblage next to angiosperm. If we compare cryptogams with phanerogams plants, in perspective of nanofabrication, cryptogams are found to be more advantageous with simple organization of the plant body. The phytochemical analysis of these primitive plants confirmed that they have a variety of biochemicals and can be used in many ways. Fabrication of metal silver and gold nanoparticles is reported from cryptogams, as portrayed in Fig. 5.3, but the bio-fabrication of platinum nanoparticles (Pt-NPs) and palladium nanoparticles (Pd-NPs) has not been explored yet. Cryptogams are imitated as powerful ion exchanger, generally bryophytes due to simple organization of the tissues have the capability of heavy metal uptake from soil and water (industrial effluents) (Tyler 1990; Zhang et al. 2004). Thus, it has been used as the sorbent for heavy metal ions and further reduction to metallic nanoparticles (Ganji et al. 2005). Cryptogams are bestowed with the capacity to uptake metal ions and converse them to corresponding nano-metallic form (Chefetz et al. 2005). Therefore, researchers have a practical interest to reveal the possibilities of nanofabrication through cryptogams.

5.3.1 *Nanofabrication Using Bryophytes*

Bryophytes are used as an experimental model system for the explication of biological processes. They exhibit several key characteristics such as ease of growth and maintenance, fast generation time (Giles 1971), DNA sequencing, and

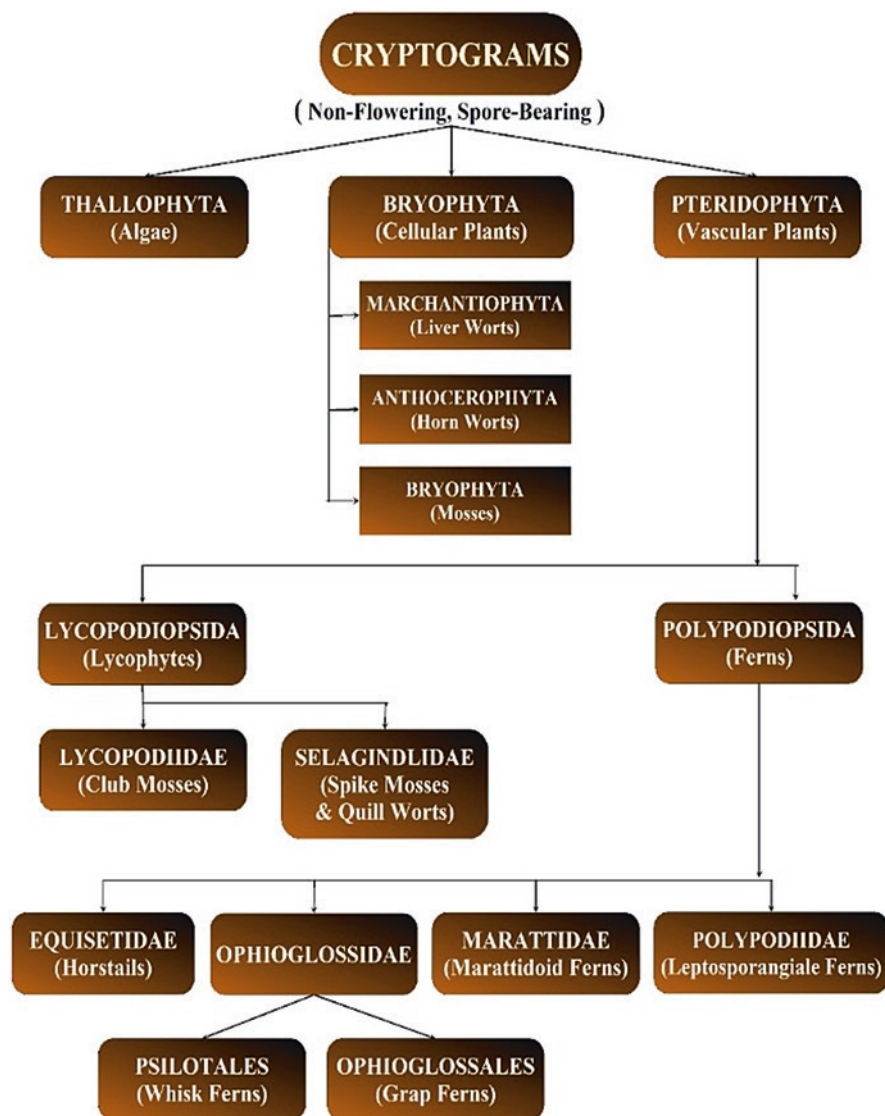


Fig. 5.2 Flow diagram of phylogenetic system

production of transgenic individuals via transformation (Wood et al. 2000). These properties prove it to be powerful model system for study of nanomaterial synthesis and their affects. The reduction of metal ions from aqueous and ethanolic extract of moss led to the formation of metal nanoparticles. Silver nanoparticles (Ag-NPs) synthesis with lower to higher (1–10 M) concentration of silver nitrate (AgNO_3) solutions was reported. Biosynthesis of Ag-NPs from a bryophyte was initially

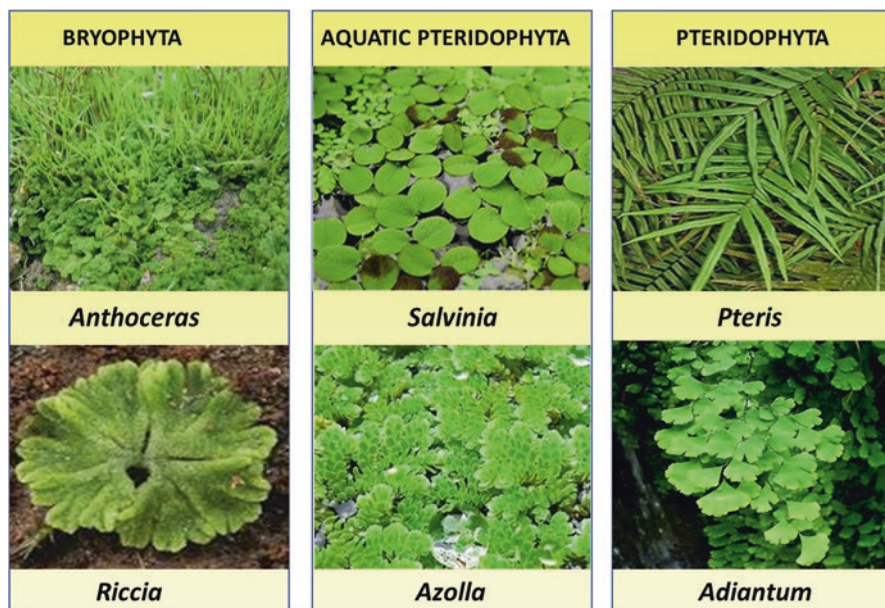


Fig. 5.3 Photograph of some species of cryptogams used in the biosynthesis

proposed by Kulkarni et al. (2011), they demonstrated that 1 mM aqueous solution of silver nitrate with aqueous filtrate of *Anthoceros* when kept at 25 °C on a shaker at 150 rpm in dark led to Ag-NPs fabrication. 1 mM aqueous solution was decided by optimizing the experiment by varying the concentration of silver nitrate from 0.5, 1, 2, 3 to 5 mM (Kulkarni et al. 2011). Later, synthesis of Ag-NPs from aqueous extract of *Fissidens minutus* with 0.5 mM silver nitrate solution at room temperature was testified (Srivastava et al. 2011). The fabrication of silver nanoparticles using aqueous extract of *Riccia* on a shaker at 150 rpm in dark at 25 °C was reported in their experiment (Kulkarni et al. 2012). Bryophytes also reduced chloroauric acid (HAuCl₄) solution to gold nanoparticles when 3 mM HAuCl₄ was treated with aqueous filtrate of *Taxithelium nepalense* (Acharya and Sarkar 2014). Silver nanoparticles production from *Bryum medianum* plant extract treated with aqueous 1 mM AgNO₃ solution at room temperature for 24 h has also been reported (Sathish et al. 2016). Similarly, aqueous filtrate of *C. flexuosus* with 1 mM AgNO₃ solution when exposed to sunlight for an hour led to Ag-NPs synthesis (Vimala et al. 2017). The bryophytes mediated synthesized particles show antioxidant property with higher degree of scavenging free radicals activity. These members of cryptogams have the ability to produce diverse types of metal and oxide nanoparticles that inhibited the pathogenic organisms (Sathish et al. 2016). These synthesized nanoparticles may combine with antibiotics to enhance their bactericidal activities (Srivastava et al. 2011).

5.3.2 Nanofabrication Using Pteridophytes

Pteridophytes have also the facility to reduce metal salt solution to metal nanoparticles due to fullness in phytochemicals. First time bio-reduction of silver nanoparticles from aquatic pteridophyte (*Azolla*) was reported by Chefetz et al., they testified that the aquatic plant *Azolla* used as the sorbent for Ag^+ , Pb^{2+} , and Ru^{3+} ions could transform them to the corresponding nano-metallic particles. Chefetz, combined two methods, adsorption of metallic ions on aquatic plants and conversion of the adsorbed heavy ions, into metallic nanoparticles. This combined process offers a hopeful approach for the removal of heavy metals from wastewater and the reutilizing of adsorbed metals into beneficiary products of metallic nanoparticles (Chefetz et al. 2005). Later, Kang et al. reported more than 85% reduction of the Ag ions is completed within 12 h, when it is synthesized from pteridophyte extract. Prepared nanoparticles remained stable for 12 months at room temperature, and there were no signs of any aggregation (Kang et al. 2008). Stability, aggregation, shape, size, and nature of nanoparticles are decided by some selected parameters; these known parameters are concentration of metal salt, pH, temperature, nature of plant extract, and reaction time. While synthesis of gold and silver nanoparticles using fern *A. philippense* L., the importance of these parameters were considered by Sant et al. According to Sant and co-workers, the optimum proportion for Au-NPs synthesized to the original plant extract was 1:1 at pH 11 with 5 mM salt concentration (tetrachloroauric acid), whereas for Ag-NPs synthesis 1:1 proportion of original plant extract at pH 12 and 9 mM concentration of silver nitrate yielded the desired results (Sant et al. 2013). The phytochemical examination of plant extract showed *Adiantum* contains terpenoids (filicene, filicenal, adiantone, isoadiantone, 23-hydroxyfernene), triterpenes (adininaonol and adininaneone), flavonoids (rutin, quercetine-3-glucaronyl, and isoquercetin), hentriacontane, 16-hentriacontanone, β -sitosterol, and fernene. The presence of these phytochemicals in *Adiantum* made it a probable candidate for bio-reduction of silver and gold salts. *Adiantum philippense* L. is known for its antioxidant potential (Sawant et al. 2009) and its ethnomedicinally significance. This fern is also used in treatment of diseases like rabies, paralysis, epileptic fits, elephantiasis, dysentery, pimples, wounds, and blood-related diseases (Karthik, et al. 2011) due to its antimicrobial activity (Pan et al. 2011). The presence of medicinal carrier, termed phytochemicals, makes them suitable candidate for biosynthesis of nanoparticles and in treatment of disease. *Adiantum capillus-veneris*-assisted Ag-NPs showed extreme toxicity against multi-drug resistant human pathogenic bacteria (Santhoshkumar and Nagarajan 2014). An aquatic fern *Azolla* sp. had been proved to have the ability to synthesize the metal (Au) as well as oxide (ZnO) nanoparticles (Jha and Prasad 2016; Asha and Francis 2015). *Azolla* has the potential to act as the stabilizing and reducing agent due to richness in phenols, tannins, sugars, flavanoids, steroids, and proteins. The aqueous extract of *Pteris* contains flavonoids (Kaempferol, Kaempferol-3-*o*-D glucopyranoside, Quercetin, and rutin) enzymes, proteins, amino acids, alkaloids, polysaccharides, phenolics, terpenoids, and vitamins, which

has the ability to convert the silver ions into silver nanoparticles (Baskaran et al. 2016). *Asplenium scolopendrium* L. mediated Ag-NPs, improved antioxidant activity as compared to frond extract, tested on the root apexes of *Allium cepa* by genotoxic assay. This may be due to adsorption of those phytochemicals, which is responsible for antioxidant activity from the extract onto the surface of the nanoparticles (Şuğan et al. 2016). Combination of nanoparticles with other nanoparticles or conjugating with drugs enhances the property of nanoparticles. Synthesized gold nanoparticles from *Adiantum philippense* extract conjugated with antibiotics were found to have a synergistic activity against microorganisms (Kalita et al. 2016). The outer surface of gold nanoparticles was shielded with β -lactam antibiotic and gold nanoparticles-amoxicillin (GNP-Amox) conjugate enhanced antibacterial activity against Gram-positive as well as Gram-negative bacteria. Besides, *in vitro* and *in vivo* assays of GNP-Amox conjugate lead to effective anti-MRSA (methicillin-resistant *Staphylococcus aureus*) activity. Hence, GNP-Amox conjugate has been used as a promising antibacterial therapeutic agent against MRSA as well as other pathogens (Ghosh et al. 2012; Kalita et al. 2016). Although these members of cryptogam family are rich in active metabolites, there are only few reports of nanoparticle fabrication by bryophytes and pteridophytes, as compared to that of higher plants. The reported fabrications are tabulated in Table 5.1.

5.4 Monitoring of Nanoparticles

Observation and monitoring of a process is paramount for new discoveries, and this is applicable for nanotechnology too. As far as nano entities are concerned one cannot proceed further with their appliance until and unless these are monitored for needful fabrication and properties. Synthesized nanoparticles are confirmed by characterization tools and monitoring of nanoparticles is worthy to understand properties of nanoparticles. Nanoparticles are usually attributed for shape, size, and over all composition. Elucidation of nanoparticles has been resolved by numerous characterization techniques under the umbrella of characterization of nanomaterials using UV-vis spectrometry, energy dispersive X-ray (EDX), X-ray diffraction (XRD), dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) as shown in Fig. 5.4. In the case of reported nanofabrication by cryptogams, primarily the change in colour of colloidal solution symbolizes fabrication of nanomaterials. Then after, results of UV-vis spectrometer confirmed the fabrication of nanomaterials by surface plasmon resonance (SPR) peak absorbance value. UV-vis spectral analyses depend on concentration of H^+ ion (pH) (Akhtar et al. 2013), metal salt concentration (Dubey et al. 2010), ratio of reactants (Sheny et al. 2011), temperature and total reaction time, which reveals the shape and size (morphology) and its stability. Sharpness in peak indicates the smaller size and broadening shows chances of agglomeration (Sant et al. 2013). When SPR peak shifted towards red, this indicates the size of particle

Table 5.1 Nanomaterials fabrication from bryophytes and pteridophytes

S. no.	Reducing agent	Nano particle	Characterization	Particle characteristics	Application	References
Bryophytes						
1	Aqueous filtrate of <i>Anthoceros</i>	Ag-NPs	UV-Vis SEM EDS	Size 20–50 nm Shape-cub/ triangular	Antibacterial action against <i>E. coli</i> , <i>B. subtilis</i> , <i>K. pneumoniae</i> , <i>P. aeruginosa</i>	Kulkarni et al. (2011)
2	Aqueous and ethanol filtrate of <i>Fissidens minutus</i>	Ag-NPs	UV-Vis SEM EDS	Shape-nearly spherical	Antibacterial action against <i>E. coli</i> , <i>B. cereus</i> , <i>K. pneumoniae</i> , <i>P. aeruginosa</i>	Srivastava et al. (2011)
3	Ethanol filtrate of <i>Riccia</i>	Ag-NPs	UV-Vis SEM EDS	Shape-cub/ triangular	Antibacterial against <i>P. aeruginosa</i>	Kulkarni et al. (2012)
4	Ethanol filtrate of <i>Anthoceros</i>	Ag-NPs	UV-Vis SEM EDS	Size 20–50 nm Shape-cub/ triangular	Antibacterial activity after incorporation into gauze cloth	Kulkarni et al. (2012)
5	Aqueous filtrate of <i>Taxithelium nepalense</i>	Au-NPs	UV-Vis, DLS, FTIR, EDX, XRD, TEM	Size range, 42–145 nm. Shape- spherical, triangular, hexagonal	N/A	Acharya and Sarkar (2014)
6	Aqueous filtrate of <i>Bryum medianum</i> Mitt.	Ag-NPs	UV-Vis FTIR, FESEM, EDX XRD	Size 85 nm shaped nanocrystals	Antimicrobial action against <i>Proteus mirabilis</i> , <i>Escherichia coli</i> , <i>Klebsiella pneumoniae</i> , <i>Aspergillus fumigatus</i> , <i>Candida albicans</i> , and <i>Trichophyton mentagrophytes</i>	Sathish et al. (2016)
7	Aqueous filtrate of <i>Campylopus flexuosus</i>	Ag-NPs	UV-Vis FTIR FESEM Zeta potential XRD	Size 51 nm Shape- spherical	N/A	Vimala et al. (2017)

(continued)

Table 5.1 (continued)

S. no.	Reducing agent	Nano particle	Characterization	Particle characteristics	Application	References
Pteridophytes (fern)						
8	Aqueous filtrate of <i>Pteridophyta</i>	Ag-NPs	UV-Vis TEM EDX	Size 20–30 nm Shape- spherical	Ag-Nps are stable for 12 months	Kang et al. (2008)
9	Aqueous filtrate of <i>Adiantum philippense</i> L.	Ag-NPs and Au-NPs	UV-Vis FTIR EDS TEM DLS XRD	Size 10–18 nm Shape- anisotropic Structure- FCC	Ag-Nps from medicinally important plants opens spectrum of medical applications	Sant et al. (2013)
10	Aqueous filtrate of <i>Cheilanthes Forinosa</i> Forsk leaf	Ag-NPs	UV-Vis SEM XRD	Size ~26.58 nm Shape- spherical Structure- FCC	Antibacterial action against <i>S. aureus</i> and <i>Proteus morgani</i>	Nalwade et al. (2013)
11	Aqueous filtrate of <i>Pteris argyreae</i> , <i>Pteris confuse</i> , and <i>Pteris biaurita</i>	Ag-NPs	N/A	N/A	Antibacterial action against <i>Shigella boydii</i> , <i>Shigella dysenteriae</i> , <i>S. aureus</i> , <i>Klebsiella vulgaris</i> , and <i>Salmonalla typhi</i>	Britto et al. (2014)
12	Aqueous filtrate of <i>Nephrolepis exaltata</i> L. fern	Ag-NPs	UV-Vis SEM XRD	Size—avg. 24.76 nm Shape- spherical Structure- FCC	Antibacterial against many human and plant pathogens	Bhor et al. (2014)
13	Aqueous filtrate of <i>Adiantum capillus-veneris</i> L.	Ag-NPs	UV-Vis SEM EDX	Size 25–37 nm Cubic structure Shape- spherical	Antimicrobial against human pathogenic bacteria such as <i>Streptococcus pyogenes</i> , <i>Staphylococcus aureus</i> , <i>Escherichia coli</i> , and <i>Klebsiella pneumonia</i>	Santhoshkumar and Nagarajan (2014)

(continued)

Table 5.1 (continued)

S. no.	Reducing agent	Nano particle	Characterization	Particle characteristics	Application	References
14	Aqueous extract of <i>Diplazium esculentum</i> (retz.) sw	Ag-NPs	UV-Vis FTIR TEM XRD	Size 9.71 nm spherical, oval, and triangular	As catalyst in degradation of methylene blue (MB) and rhodamine B (RhB) dyes under solar light illumination	Paul et al. (2015)
15	Aqueous filtrate of <i>Pteris tripartita</i> Sw.	Ag-NPs	UV-Vis SEM TEM, XRD, EDX, FTIR	Size 32 nm hexagonal, spherical, and rod-shaped structures	Antibacterial against 12 different bacteria, antifungal against five different fungus, in vitro antioxidant, in vivo anti-inflammatory activities	Baskaran et al. (2016)
16	Ethanollic extracts of <i>Asplenium scolopendrium</i> L.	Ag-NPs	UV-Vis EDXRF FTIR	Size—below 50 nm	Antioxidant activity and genotoxic effects of the extracts on the root apexes of <i>Allium cepa</i>	Şuğan et al. (2016)
17	Aqueous extract of <i>Dicranopteris linearis</i>	Ag-NPs	UV-vis, FTIR SEM, EDX, XRD, zeta potential, and particle size analysis	Size—about 40–60 nm in diameter spherical in shape	Mosquitocidal assays, Smoke toxicity against <i>A. aegypti</i>	Rajaganesh et al. (2016)
Pteridophytes (aquatic fern)						
18	Aqueous solution of <i>Azolla filiculoides</i>	Ag-NPs	XRD, TEM	Size 20–30 nm spherical	N/A	Chefetz et al. (2005)
19	Aqueous extract of <i>Azolla</i>	ZnO-NPs	UV-vis spectroscopy, XRD, SEM, and FTIR	Size 19 nm spherical in shape	Antioxidant activity Antibacterial agent against <i>S. aureus</i>	Asha and Francis (2015)

(continued)

Table 5.1 (continued)

S. no.	Reducing agent	Nano particle	Characterization	Particle characteristics	Application	References
20	Ethanollic extract of <i>Azolla</i>	Au-NPs	XRD, TEM	Size 10–50 nm spherical shape	N/A	Jha and Prasad (2016)
21	Aqueous extract of <i>Salvinia molesta</i>	Ag-NPs	FESEM, HRTEM, AFM, EDX, XRD, AES	Size 12 nm spherical in shape	Antibacterial agent against both Gram-positive and Gram-negative bacteria	Verma et al. (2016)

increase and blue shift for decrease in size (Asha and Francis 2015). The morphology of fabricated nanomaterial by cryptogams and their particle shape and size were determined by SEM, TEM, and AFM. Spherical Ag-NPs were fabricated by the cryptogams like *Pteris*, *Cheilanthes forinosa*, *Diplazium esculentum*, and *Salvinia molesta* (Nalwade et al. 2013; Paul et al. 2015; Baskaran et al. 2016; Verma et al. 2016). Besides this rod-shape, hexagonal, oval shape, triangular and cuboidal shape were also reported from *Pteris*, *Diplazium esculentum*, *Anthoceros*, respectively. (Kulkarni et al. 2012; Paul et al. 2015; Baskaran et al. 2016).

AFM are superior over traditional microscopes like SEM and TEM as it enables measurement of three-dimensional structure of NPs. Particles height and volume can also be calculated through AFM. X-ray diffractometer (XRD) reveals molecular, atomic phase identification of crystalline structure of NPs. In literature, cryptogams mediated nanofabrication XRD analysis has been used to predict crystallinity of the particles. EDS or EDAX are used for analysing elemental composition of the nanomaterials. Dynamic light scattering (DLS) rectifies particle size distribution. The surface chemistry and functional (biological) groups that bound distinctively on surface of particles and were involved in the synthesis of these nanoparticles are determined by FTIR spectroscopy. In the present scenario, use of some of these characterization tools for nanoparticles fabricated by cryptogams is yet to be applied. In the near future, the increasing demand for development of fabrication processes through these cryptogams will ensure their applicability. A generalized flow chart predicting the characterization techniques is displayed in Fig. 5.4.

5.5 Probable Biosynthetic Mechanism

Biosynthesis of nanoparticles from cryptogams is currently under exploration. These cryptogams are known as lower plant and shows similarities to higher plants in some of the aspects. In the framework of nanofabrication, understanding the underlying mechanism is of paramount interest. Till date, as per the literature survey there are no reports elucidating this aspect of nanofabrication from bryophytes and

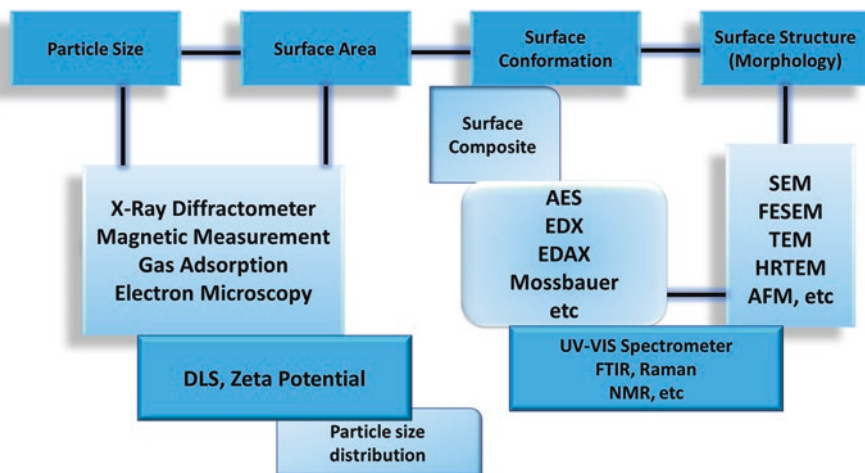


Fig. 5.4 A generalized flow chart predicting the characterization techniques

pteridophytes. The phyto-constituents present in these members of the family cryptogams have been found to be similar to that of higher plants. Hence, herein an attempt has been made to predict the probable mechanism underlying it by virtue of the mechanistic aspect reported for the higher plants. The mechanism process and pathway for nanofabrication are imprecise, even for higher plants. Prediction of exact mechanism faces several problems due to variation in phytochemical composition (Ahmed et al. 2014). However, some researchers reported the role of phenolic acid, flavonoids, terpenoids, proteins, organic acid, essential oils, etc. for synthesis and stabilization (Basha et al. 2010; Tamuly et al. 2014; Prasad 2014). These phytochemicals are also found in bryophytes and pteridophytes (Asakawa 2007; Kumari et al. 2011) rendering them the capability of nanofabrication. Limited reports are existing, where phytochemicals are directly utilized for the metallic nanoparticles synthesis (Singh et al. 2010; Ahmed et al. 2014; Durai et al. 2014; Iram et al. 2014; Dauthal and Mukhopadhyay 2016). These reports provide a clue for future endeavours employing bryophytes and pteridophytes for extraction of phytochemicals for nanofabrication. Flavonoids have the ability to donate hydrogen atom (Pietta 2000; Zhou et al. 2010) through keto-enol conversion. Consequently, these flavonoids compel the reduction of metal ions to corresponding metal nanoparticles (Ahmad et al. 2010). Similarly, hydroxyl groups (OH^-) of flavonoids (quercetin) reacts to carbonyl groups ($\text{C}=\text{O}$) during bio-reduction (Ghoreishi et al. 2011). Synthesis of Ag-NPs supported by intermediate complex in which phenolic hydroxyl groups consequently undergo oxidation to quinone with subsequent reduction of silver ions to Ag-NPs has been reported (Edison and Sethuraman, 2012). The polyphenolic compounds are capable of chelating many kinds of metallic ions (Pt^{4+} , Au^{3+} , Pd^{2+} , Ag^+ , etc.) (Mohsen and Ammar 2009). The phenolic compounds have higher antioxidant potential and it reduces metal ions into stable metal nanoparticles, thus favouring the stabilization of nanoparticles. Terpenoids also play a role as bio-reducing agent for

fabrication of Au-NPs and Ag-NPs (Singh et al. 2010). Proteins can also reduce metal silver ions to metallic NPs for example; tryptophan has reductive properties by the release of an electron during conversion of the tryptophan residue (Adyanthaya and Sastry 2004; Si and Mandal 2007). Tan et al. have tested the reducing and binding ability of twenty amino acids with metal ions (Tan et al. 2010). Tyrosine reduces gold ions and forming of stable gold nanoparticles (Roy et al. 2014). Researchers theorized the involvement of proteins in bio-reduction. Metal ions can be reduced by organic acid (alkaloid) by release of reactive hydrogen (Tamuly et al. 2014). Ascorbic acid is an effective reducing agent for the stabilization of Ag-NPs. The keto-enol tautomerization of anthroquinones is conjectured by Jha et al. (2009) for reduction of metal ions. Phytochemical examination of cryptogams reveals the presence of carbohydrates, phenols, alkaloids, steroids, terpenoids, hydroxy-hyprnone, catecholamines, tannins, saponins, anthraquinones, coumarins, fats, enzymes (NADP reductase), proteins, functional groups (amines and ketones), essential oils, flavonoids, glycosides, gums, iridoids, and mucilage (Asakawa 2007; Santos et al. 2010; Kumari et al. 2011; Suganya et al. 2011; Rai et al. 2016). As per our assumption, similar

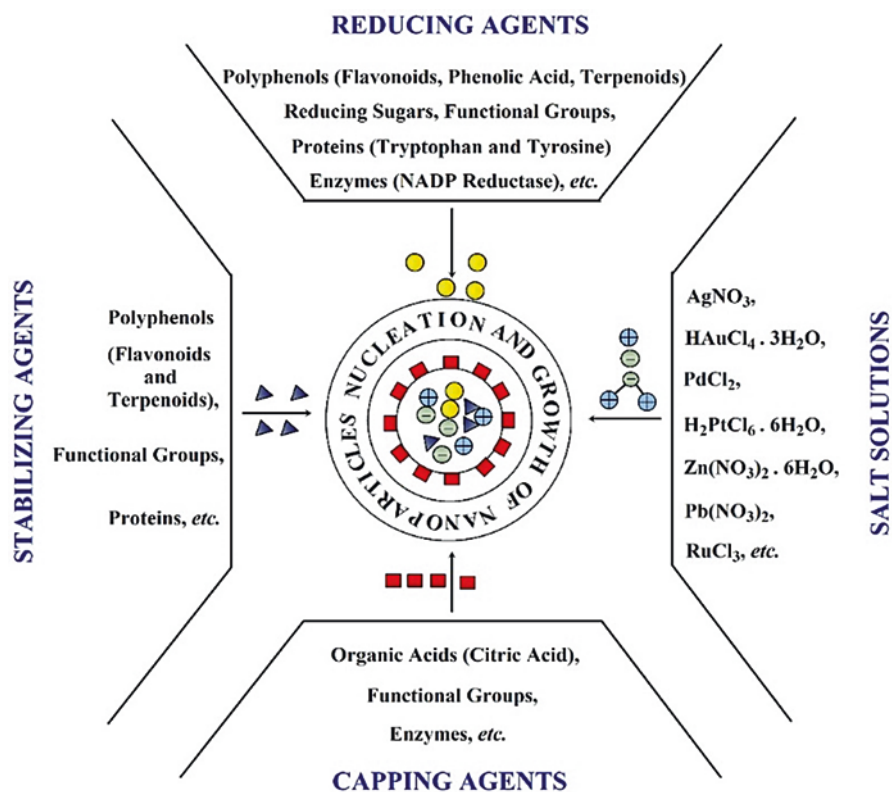


Fig. 5.5 Schematic diagram presenting probable mechanisms behind the formation of nanoparticles

bioactive compounds which are present in the extracts of cryptogams, act as a reducing as well as a stabilizing agent. Flavonoids and terpenoids act as stabilizing agent; proteins, enzymes, and functional groups act as capping agent and protein, reducing sugars, enzymes (NADP reductase), phenolic compounds, flavonoids (quercetin) as reducing agent (Akhtar et al. 2013). Thus, we can conclusively remark the participation of phytochemicals in bio-reduction of metal ions to their corresponding nanoparticles. This probable mechanism is schematized in Fig. 5.5 wherein potential reducing, stabilizing, and capping agents that are present and responsible for nano-transformation by cryptogams are indicated.

5.6 Pharmacological Applications

Nano systems and biological components both exhibiting nanometre dimensions provide probable synergies amidst them. This very fact gives implications of the foreseeable appliance of nano entities for understanding the biological processes and as nanomedicine in biomedical field. Nanoprobes or sensors for disease detection, nano systems with large surface area as drug carriers and nanodrugs as alternative to conventional drugs turn up as a precise, controllable, reliable, cost-effective, and

Table 5.2 Applications of different nanoparticles synthesized from cryptogams

Medium sources	Nanoparticles	Applications	References
(Bryophytes) <i>Anthoceros</i> , <i>Bryum medianum</i> Mitt., <i>Fissidens minutus</i> , <i>Riccia</i> , <i>Campylopus flexuosus</i> (Pteridophytes) <i>Pteridophyta</i> , <i>Adiantum philippense</i> L., <i>Adiantum capillus-veneris</i> L., <i>Cheilanthes forinosa</i> , <i>Pteris argyraea</i> , <i>Pteris confuse</i> , <i>Pteris biaurita</i> , <i>Nephrolepis exaltata</i> L., <i>Diplazium esculentum</i> (retz.) sw, <i>Pteris tripartita</i> Sw., <i>Asplenium scolopendrium</i> L, <i>Dicranopteris linearis</i> , <i>Azolla filiculoides</i> , <i>Salvinia molesta</i>	Ag-NPs	Antibacterial activity Antifungal activity Antioxidant activity Anti-inflammatory activity Larvicidal Activity Genotoxic activity Catalytic activity	Kulkarni et al. (2012, 2011), Srivastava et al. (2011), Sathish et al. (2016), Vimala et al. (2017), Kang et al. (2008), Sant et al. (2013), Nalwade et al. (2013), Britto et al. (2014), Bhor et al. (2014), Santhoshkumar and Nagarajan (2014), Paul et al. (2015), Baskaran et al. (2016), Şuţan et al. (2016), Rajaganesh et al. (2016), Verma et al. (2016), Chefetz et al. (2005)
<i>Taxithelium nepalense</i> (Bryophytes) <i>Adiantum philippense</i> L., <i>Azolla</i> (Pterodophytes)	Au-NPs	Potential medical applications	Acharya and Sarkar (2014), Sant et al. (2013), Jha and Prasad (2016)
<i>Azolla</i>	ZnO-NPs	Antioxidant activity Antibacterial activity	Asha and Francis (2015)

rapid diagnostic and treatment solution (Prasad et al. 2014, 2017). In the framework of nanoparticles fabricated by cryptogams, there are several reports wherein these particles have been tested for the pharmacological applications. The results were agreeable and indicative of the fact that these metabolite-rich cryptogams probably add on to pharmacological efficiency of bare nanoparticles. An insight to the pharmacological applications of cryptogam-mediated nanoparticles is illustrated in the following sections and summarized in Table 5.2.

5.6.1 *Antimicrobial Activity*

According to several scientific reports, it has been evidenced that nanoparticles (NPs) are highly effective against the pathogenic microorganisms like viruses, fungi, Gram-negative, and Gram-positive bacteria (Rai et al. 2012; You et al. 2012; Rizzello and Pompa 2014; Aziz et al. 2014, 2015, 2016; Joshi et al. 2018). It also exhibits bactericidal and inhibitory effects. By virtue of this property, it is widely used as an antimicrobial agent. Zone of inhibition is a very common method, which is being used to assess the antimicrobial activity of NPs (Ortiz et al. 2017). The mechanism of nanoparticles antimicrobial effect is yet to be explored. Among the nanoparticles, silver nanoparticles are widely studied for antimicrobial activity due to its medicinal history. Few researchers testified that Ag-NPs may bound to the surface of the cell membrane and interact with the disulphide bonds of the glycoprotein of microorganisms (viruses, bacteria, and fungi) instigating change in three-dimensional structures of proteins, which causes blocking the functional operations of the microorganism (Amro et al. 2000; Kim et al. 2007; Morones et al. 2005; Rai and Bai 2011; Aziz et al. 2015, 2016). In spite of interacting with the surface membrane, silver nano particles can penetrate inside the bacteria and destruct on genetic level. It may also form reactive oxygen species which interacts and damages the ATP assembly of respiration. Silver nanoparticles can also accumulate inside the cells of microbes causing damage to cell. Hence, by virtue of this mechanism, it is an effective antimicrobial agent (Rai et al. 2009; Sadeghi and Gholamhoseinpoor 2015). Some researchers have also reported that the Gram-positive bacteria are more sensitive to Ag-NPs than the Gram-negative and vice versa (Wrotniak et al. 2014; Perito et al. 2016; Dakal et al. 2016). This is very contradictory part of antibacterial action. This difference in sensitiveness is due to the difference in structure (shape and size) and methodology applies during the synthesis process of Ag-NPs. are more sensitive than spherical followed by rod shape (Xiu et al. 2012). Smaller size of Ag-NPs shows better antibacterial result. It is a well-known fact that resistant to antibiotics is found to be more in Gram-negative bacteria as compared to the Gram-positive. This resistance is mainly due to the differences in their cell wall composition. It is also revealed by the several studies that susceptibility to the cryptogams is found more in Gram-negative bacteria. This susceptibility is mainly because of the presence of broad spectrum of

antibiotic compounds present in the ferns. So, it can be said that cryptogams mediated Ag-NPs are susceptible against Gram-negative bacteria.

Fissidens minutus (bryophytes)-assisted Ag-NPs as investigated showed susceptibility against *Bacillus subtilis*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, and *Escherichia coli* (Srivastava et al. 2011). *Anthoceros*-assisted Ag-NPs showed positive result against four pathogenic strains: *Klebsiella pneumoniae*, *Escherichia coli*, *Bacillus subtilis*, and *Pseudomonas aeruginosa* (Kulkarni et al. 2011). *Bryum medianum*-mediated synthesized Ag-NPs showed greater inhibitory effect on the bacteria *Klebsiella pneumoniae* and *Escherichia coli* than *Proteus mirabilis* (Sathish et al. 2016). The growth of *Klebsiella pneumoniae* NCIM 2719, *Proteus morgani* NCIM 2719, *Corynebacterium diphtheriae*, *Pseudomonas testosteroni* NCIM 5098, *Bacillus subtilis* NCIM 2063, *Escherichia coli*, and *Xanthomonas axonopodis* pv. *punicae* were highly inhibited by the Ag-NPs synthesized using extract of a fern *Nephrolepis exaltata* L. The highest inhibitory activity was recorded for *Xanthomonas axonopodis* pv. *punicae* and lowest for *Pseudomonas teststeroni* NCIM 5098 (Bhor et al. 2014). The Ag-NPs obtained from *Adiantum capillus-veneris* also disclosed antibacterial activity against four bacterial strains: *Staphylococcus aureus*, followed by *Streptococcus pyogenes*, *Escherichia coli*, and *Klebsiella pneumoniae* than standard drugs (standard antibiotic erythromycin) (Santhoshkumar and Nagarajan 2014). Up to 3 mM zone of inhibition was found against Gram-positive bacterial strain (*S. aureus*) by *Azolla*-assisted ZnO-NPs (Asha and Francis 2015). Another source of Ag-NPs fabrication aquatic fern: *Salvinia molesta* was also explored to be a very effective antibacterial agent against Gram-negative as well as Gram-positive bacteria (Verma et al. 2016). Ag-NPs, which are produced from *Pteris tripartita* Sw. showed a positive antibacterial action against as much as 12 different bacterial strains. Experiment was accomplished by disc diffusion, time course growth methods, and minimum inhibitory concentration (MIC). The studies regarding in vivo (anti-inflammatory) and in vitro (antimicrobial and antioxidant) are also carried out for Ag-NPs. Ag-NPs also showed anti-inflammatory activity. This activity is well explained through carrageenan-induced paw volume experiment in female Wistar albino rats (Baskaran et al. 2016).

5.6.2 Antifungal Activity

Ag-NPs are found to be effective fungicides against common fungi such as *Candida*, *Aspergillus*, and *Saccharomyces* (Yu et al. 2005). *Bryum medianum*-assisted synthesized Ag-NPs also showed antifungal activity; the highest degree of inhibition was observed in *Candida albicans* in comparison to *Aspergillus fumigatus* and *Trichophyton mentagrophytes* (Sathish et al. 2016). Ag-NPs obtained from *Pteris tripartita* Sw. was found to exhibit antifungal activity against four different species. It showed positive antifungal activities against *Fusarium oxysporum*, *Rhizopus oryzae*, *Aspergillus niger*, and *Aspergillus flavus* (Baskaran et al. 2016).

5.6.3 Larvicidal Activity

The Ag-NPs are known to show the larvicidal activity by killing the larvae of vectors at an early stage (Buhroo et al. 2017). Many Ag-NPs have shown larvicidal activity against malarial vectors *Aedes aegypti* (Suresh et al. 2014). Metal nanoparticles, especially Ag-NPs, show maximum larvicidal activity. Silver nanoparticles fabricated using leaf extract of *Dicranopteris linearis* were testified that it has larvicidal activity against *A. aegypti* adults, egg hatchability reduced by 100% when treated with 25 ppm of Ag-NPs. Ag-NPs reduced oviposition rates more than 70%. One of the useful applications of *D. linearis*-mediated Ag-NPs is to develop nano-formulated oviposition deterrents, which is effective against dengue vectors (Rajaganesh et al. 2016).

5.6.4 Wound Healing Activity

The Ag-NPs showed wound healing activity. It can penetrate into the fibroblast cells and accrued over time, at the same time it does not interfere with the cell viability. During apoptosis, the mitochondria are activated in the cell to reduce its viability (Garg et al. 2014). The wound-healing application of Ag-NPs has already been tested on animal models (Arunachalam et al. 2013). This fact gives an idea that cryptogam-mediated Ag-NPs can also be used for wound healing activity.

5.6.5 Medicinal Textiles

In the field of Textiles, NPs may enhance the quality of fabric. Kulkarni et al. testified antimicrobial activity against *Pseudomonas aeruginosa* of gauze cloth in disc form incorporated with Ag-NPs, which is synthesized from *Anthoceros* (Kulkarni et al. 2012).

5.6.6 Catalytic Activity

Diplazium esculentum-mediated Ag-NPs were also used as catalyst in degradation of dyes. Rhodamine B (RhB) and methylene blue (MB) dyes degradation under solar light in the presence of Ag-NPs was checked for analysis of its catalytic efficiency. The discolouration of dyes occurred in minutes, indicative of the fact that small-sized Ag-NPs caused structural changes and depletion of chromophoric group

from the dye. The pronounced photocatalytic activity of Ag-NPs was attributed to its small size achieved through the bio-reductive process (Paul et al. 2015).

5.6.7 Antioxidant Activity

The presence of free radicals in cells is responsible for the development of many diseases like cancer, cardiovascular Alzheimer's atherosclerosis, diabetes, and ageing (Coyle and Puttfarcken 1993). Therefore, evaluation of the free radical scavenging potential of biosynthesized nanoparticles supports in the treatment of such diseases. *Bryum medianum* moss plant-mediated Ag-NPs antioxidant activity as determined by the DPPH assay showed the higher percentage of inhibition compared to the ascorbic acid. Thus, Ag-NPs obtained from *Bryum medianum* have the potential to scavenge the free radicals (Sathish et al. 2016). Baskaran et al. also reported in vitro antioxidant activities of Ag-NPs derived from *Pteris tripartita* by DPPH radical scavenging method, hydrogen peroxide scavenging method, and azinobis 3-ethylbenzothiazoline-6-sulfonate (ABTS⁺) assay. (Baskaran et al. 2016). Similarly, Şuğan et al. from ethanolic extracts of *A. scolopendrium* L. obtained Ag-NPs and compared it for the genotoxic effect on the root apexes of *Allium cepa*. The finding showed that Ag-NPs synthesized using the extract of *A. scolopendrium* L. enhanced the antioxidant activity as compared to the extract. Enhancing of antioxidant activity may be attributed to small size and adsorption of antioxidant components from the extract to the surface of the nanoparticles thereby increasing its efficiency (Şuğan et al. 2016).

5.6.8 Cytotoxicity

Cancer is a life-threatening disease and its treatment is lethiferous. Nanotechnology turns up as a novel approach for the treatment of cancer because of its lesser side effects compared to conventional chemotherapy and synthetic drugs. Nanoparticles as reported by several researchers have anticancer potential. It is anti-proliferative (Firdhouse and Lalitha 2013), apoptosis inducer (Mukherjee et al. 2015), anti-metastatic (Karuppaiya et al. 2013), and has cytotoxic effect (Suman et al. 2013). The cytotoxicity studies of green synthesized NPs on different mammalian cell lines are usually convoyed with quantitative cell viability via MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) and qualitative viability through death double staining, acridine orange, and ethidium bromide live assays (Sukirthaa et al. 2012; Ramamurthy et al. 2013; Preethi and Padma 2016). The outcome from all those current research is that cytotoxic activity was tremendously sensitive to the size of the nanoparticles and the viability capacities decreased with increasing dosage. Thus, cryptogams mediated nanoparticles could be used as anticancer agent. The potential of such medicinally important lower plants can be used for the development of new anticancer drugs.

5.7 Conclusion

The developing era of nanoscience is a famous flair for the development of science all over the world. With the advent of application of nanoparticles in almost every field, the need for an inexpensive, eco-friendly, simple process of fabrication is of core interest. Several studies have been done over the last decade on application of biological entities as nanofabricators starting from microbes to higher plants, but there are still significant openings in our knowledge wherein groups like cryptogams have not been explored judiciously. These cryptogams have been gifted with immense reservoir of active metabolites with bio-reductive and pharmacological potentials. This chapter summarizes information about the nanofabrication by cryptogams and its scope in pharmacological actions. Moreover, in order to have better understanding general description about cryptogams has also been included. In framework of nanofabrication, the bryophytes and pteridophytes remain largely unexplored and unattended, with reports in scratches. The chapter describes the various possibilities and benefits with intent to draw attention towards these members for nanofabrication explorations. Further, it has stressed on the need to determine the phytochemical constituents of the extract, as well as to find out the mechanism responsible for synthesis. Conclusively, this chapter is an attempt to explore the unexplored members of plant diversity, the cryptogams for fabrication of nanoparticles.

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Chapter 6

Plant and Its Biomolecules on Synthesis of Silver Nanoparticles for the Antibacterial and Antifungal Activity



S. Rajeshkumar, R. V. Santhiyaa, and P. Veena

6.1 Introduction

Silver nanoparticles are used in different biomedical applications such as antifungal, antibacterial, anti-inflammatory, antidiabetic, and anticancer applications. The silver nanoparticles synthesized using different natural resources such as bacteria *Klebsiella planticola* (MTCC 2277), *Vibrio alginolyticus*, *Enterococcus* sp., *Serratia nematodiphila*, *Bacillus* sp., *Phaenerochaete chrysosporium*, *Bacillus licheniformis*, *Escherichia coli*, *Corynebacterium glutamicum*, *Planomicrobium* sp., and *Bacillus subtilis* MTCC 3053 (Rajeshkumar 2016a; Rajeshkumar and Bharath 2017), fungus such as *Trichoderma viride* (5–40 and 2–4 nm), *Aspergillus flavus*, *Aspergillus fumigates*, *Verticillium* sp., *Fusarium oxysporum*, and *Neurospora crassa* (Li et al. 2011). The major application of silver nanoparticles is antimicrobials (Aziz et al. 2014, 2015, 2016). The antimicrobial silver nanoparticles are used in different types of products in detergents, textiles and clothing, the work surfaces and kitchen surface coating, medical implants with Poly(*N*-vinyl pyrrolidone), wastewater treatment and purification of drinking water, food preservation (controlling foodborne pathogens), health supplements, deodorants and washing machines like household items, paints, etc. (Sweet and Singleton 2011).

The plants are the major natural resource used for the environmentally benign silver nanoparticles synthesis, which is shown in Fig. 6.1. Especially the plant parts such as leaves (majorly used for the AgNPs synthesis), flower, fruits, seeds, bark, stem, peels, and sometimes whole plant have been used for the green synthesis of

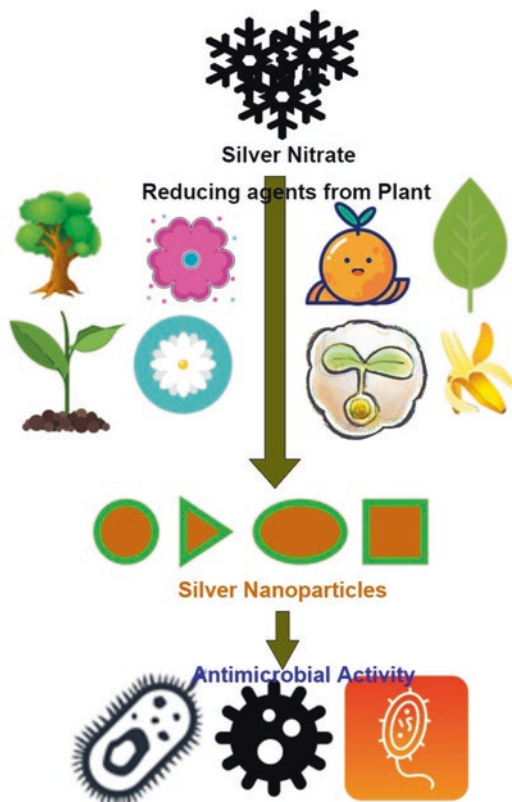
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Fig. 6.1 Plant-mediated synthesis of silver nanoparticles



silver nanoparticles described in Tables 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, and 6.9. The surface plasmon resonance analyzed using UV-vis spectrophotometer, size and shape analyzed using scanning electron microscope and transmission electron microscope, and the phytochemicals present in the plant extract responsible for AgNPs synthesis are depicted in Tables 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, and 6.9. The different shapes of silver nanoparticles synthesized using plant sources are mentioned in Fig. 6.2. The different functional groups involved in the synthesis of silver nanoparticles are shown in Fig. 6.3.

In recent times, the plant-mediated synthesis of nanoparticles is an emerging out process in the field of nanobiotechnology owing to its several advantages. Various parts of plants such as leaf, stem, root, flower, fruit, and seed were utilized for the synthesis of nanoparticles. Other than the plant-related parts, the waste materials related to the plants were also used for the synthesis of the nanoparticles like hull, peel, and seed of the fruits. The biological compounds in the plant parts were involved in the synthesis of nanoparticles by acting as the reducing as well as capping or stabilizing agent during the synthesis of silver nanoparticles. There is no additional reducing agent added in the green synthesis of nanoparticles. Especially, the existences of phytochemicals like flavonoids, saponins, tannins, terpenoids, and phenols in the plant

Table 6.1 Leaves-mediated synthesis of silver nanoparticles

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
1	<i>Phyllanthus amarus</i>	420	30–42	Flower-like structure	The biomolecules (carbonyl, hydroxyl, alkanes, and amine) present in the leaf extract were responsible for the formation and stabilization of nanoparticles	Ajitha et al. (2018)
2	<i>Nigella arvensis</i>	416	5–100	Spherical	The phytochemicals such as flavonoids, alkaloids, and phenols perform a dual as reducing and stabilizing agent	Chahardoli et al. (2018)
3	<i>Melia azedarach</i> L.	482	34–48	Spherical	–	Mehmood et al. (2017)
4	<i>Calliandra haematocephala</i>	414	70	Spherical	The biomolecules especially gallic acid present in the leaf performed a major role as reducer and stabilizer	Raja et al. (2017)
5	<i>Cassia roxburghii</i>	473	15–20	Spherical	The presence of potential bioactive molecules such as alcohols, carboxylates, amines, alkanes, and alkynes act as both reduction and stabilization agent	Moteriya et al. (2017)
6	<i>Skimmia laureola</i>	460	46	Spherical	The biomolecules present in the leaf such as skimmidiol, coumarins, and triterpenoids performed as reducing and stabilizing agent	Jamil et al. (2015)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
7	<i>Convolvulus arvensis</i>	430	28	Spherical	The potent bioactive molecules such as organic acids, phenols, and aliphatic amines in the leaf act as a reducing and stabilizing agent for the synthesis of metal ions	Hamedi et al. (2017)
8	<i>Ficus religiosa</i>	421	21	Spherical	The biological compounds present in the leaf of <i>Ficus religiosa</i> may be involved in the reduction and capping in the process of synthesis of NPs	Nakkala et al. (2017)
9	<i>Adhatoda vasica</i>	450	10–50	Spherical	The functional groups like amides, amino acids, carboxyl and amino groups present in the leaf extract act as reducing and stabilizing agent	Latha et al. (2016)
10	<i>Physalis angulata</i>	436	11–96	Spherical	The proteins, amino acids, and phenolic groups were responsible for the synthesis of NPs as stabilizing and reducing agent	Kumar et al. (2017b)
11	<i>Lantana camara</i> L.	439	410–450	Spherical	The presence of carboxylic, hydroxyl, phenyl, and carbonyl groups was important for the reduction and stabilization process in the synthesis of NPs	Patil Shrinivas and Kumbhar Subhash (2017)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
12	<i>Marsilea quadrifolia</i>	435	9–42	Spherical	The phenolic compounds, tannins, sugars, alkaloids, and flavonoids present in the leaf of <i>M. quadrifolia</i> might have been used as a reduction and capping agent	Maji et al. (2017)
13	<i>Olive</i>	440–458	20–25	Spherical	The presence of functional groups in the olive leaf was responsible for the synthesis of nanoparticles	Khalil (2013)
14	<i>Tinospora cordifolia</i>	430	24	Spherical	The biological moieties present in the leaf extract play a dual role in the reducing and stabilizing agent	Selvam et al. (2017)
15	<i>Andrographis echioidea</i>	426	–	–	The biomolecules like phenolic groups, lipids, and proteins present in the leaf extract of <i>A. echioidea</i> act as a reduction and stabilization agent in the synthesis of silver NPs	Elangovan et al. (2015)
16	<i>Sesuvium portulacastrum</i>	420	5–20	Spherical	The silver nanoparticles can be synthesized by the extract of callus and leaf of <i>S. portulacastrum</i> due to its excellent reducing and stabilizing property	Sesuvium et al. (2010)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
17	<i>Artemisia vulgaris</i>	420	25	Spherical	The functional groups such as carbonyl, phenols, and aromatic amine present in the phytochemicals of leaf extract might have been acting as a stabilizing and reducing agent for the synthesis of NPs	Rasheed et al. (2017)
18	<i>Ceropegia thwaitesii</i>	430	100	Spherical	The presence of methoxy group, triterpenoids, vinyl, carbonyl, and secondary amine in the leaf extract of <i>C. thwaitesii</i> was responsible for the capping and reduction of silver NPs	Muthukrishnan et al. (2014)
19	<i>Lantana camara</i>	421	37–29	Spherical	The phytochemicals present in the leaf extract of <i>Lantana camara</i> were responsible for the reduction of silver NPs and stabilization	Ajitha et al. (2015)
20	<i>Bryophyllum pinnatum</i>	447	15–40	Spherical	The presence of protein residues in the leaf extract act as a reducing as well as stabilizing agent for the synthesis of silver NPs	Kabir et al. (2017)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
21	<i>Alternanthera dentata</i>	430	50–100	Spherical	The biomolecules present in the extract act as a reducing and capping agent. Thus, the FTIR also confirms that the existence of soluble water fractions in the leaf extract affects the formation of silver NPs	Ashok et al. (2014)
22	<i>Andrographis echiioides</i>	426	–		The biomolecules like phenolic groups, lipids, and proteins present in the leaf extract of <i>A. echiioides</i> act as a reduction and stabilization agent in the synthesis of silver NPs	Elangovan et al. (2015)
23	<i>Sesuvium portulacastrum</i>	420	5–20	Spherical	The silver nanoparticles can be synthesized by the extract of callus and leaf of <i>S. portulacastrum</i> due to its excellent reducing and stabilizing property	Sesuvium et al. (2010)
24	<i>Artemisia vulgaris</i>	420	25	Spherical	The functional groups such as carbonyl, phenols, and aromatic amine present in the phytochemicals of leaf extract might have been acting as a stabilizing and reducing agent for the synthesis of NPs	Rasheed et al. (2017)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
25	<i>Ceropegia thwaitesii</i>	430	100	Spherical	The presence of methoxy group, triterpenoids, vinyl, carbonyl, and secondary amine in the leaf extract of <i>C. thwaitesii</i> was responsible for the capping and reduction of silver NPs	Muthukrishnan et al. (2014)
26	<i>Lantana camara</i>	421	37–29	Spherical	The phytochemicals present in the leaf extract of <i>Lantana camara</i> were responsible for the reduction of silver NPs and stabilization	Ajitha et al. (2015)
27	<i>Bryophyllum pinnatum</i>	447	15–40	Spherical	The presence of protein residues in the leaf extract act as a reducing as well as stabilizing agent for the synthesis of silver NPs	Kabir et al. (2017)
28	<i>Alternanthera dentata</i>	430	50–100	Spherical	The biomolecules present in the extract act as a reducing and capping agent. Thus, the FTIR also confirms that the existence of soluble water fractions in the leaf extract affects the formation of silver NPs	Ashok et al. (2014)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
29	<i>Artocarpus altilis</i>	432	34 and 38	Spherical	The presence of phytoconstituents in the leaf extract act as stabilizing and capping agent for the synthesis of silver nanoparticles	Ravichandran et al. (2016)
30	<i>Mimusops elengi</i> L.	434	55–83	Spherical	The presence of biomolecules in the leaf extract of <i>M. elengi</i> has an ability to reduce and stabilize nanoparticles	Prakash et al. (2013)
31	<i>Euphorbia hirta</i>	425	15.5	Spherical	The presence of polyphenolic compounds and protein act as both reducing and stabilizing agents	Kumar et al. (2017b)
32	<i>Ananas comosus</i>	440–460	12.4	Spherical	The functional groups such as methoxy group and carbonyl group present in the biomolecules of leaf extract act as an excellent reducing and stabilizing agent	Elias et al. (2014)
33	<i>Acalypha indica</i>	420	20–30	Spherical	–	Krishnaraj and Jagan (2010)
34	<i>Sesbania grandiflora</i>	416	16	Well-dispersed and spherical shape	The FTIR analysis reveals that the leaf extract of <i>S. grandiflora</i> might have been acting as capping and reducing agent	Ajitha et al. (2016)
35	<i>Hemidesmus indicus</i>	430	25.24	Spherical	The bioactive molecules in the leaf extract of <i>H. indicus</i> maybe act as a reducing and stabilizing agent	Latha et al. (2015)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
36	<i>Rosmarinus officinalis</i>	450	10–33	Spherical	The functional groups of phenolic compounds in the leaf extract might have been acting as a reducing and stabilizing agent in the synthesis of silver nanoparticles	Ghaedi et al. (2015)
37	<i>Croton sparsiflorus Morong</i>	457	22–52	Spherical	The FTIR study exhibits that the functional groups such as carboxyl, amine, hydroxyl, aldehydes, and ketones in the leaf extract exhibit double functional role as reducing and stabilizing agent	Kathiravan et al. (2015)
38	<i>Atalantia monophylla</i>	404	35	Spherical	The functional groups of aromatic compounds in the leaf extract act as a reducing and stabilizing agent	Mahadevan et al. (2017)
39	<i>Ocimum tenuiflorum</i>	450	25–40	Spherical	Leaf extract of <i>O. tenuiflorum</i> acts as reducing and capping agent for the synthesis of nanoparticles	Patil et al. (2012)
40	<i>Xanthium strumarium</i>	436	12–20	Spherical	The phenolic compounds in the leaf extract act as both reducing and stabilizing agent	Kumar et al. (2016b)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
41	<i>Mukia maderaspatana</i>	430	58–458	Spherical	The leaf of <i>M. maderaspatana</i> has a rich source of phenolic compounds which are used as a reducing agent during the synthesis of nanoparticles	Harshiny et al. (2015)
42	<i>Psidium guajava</i> L.	435	25–35	Spherical	The presence of polysaccharides in the leaf extract act as reducing and stabilizing agent for the synthesis of nanoparticles	Wang et al. (2017)
43	<i>Salvinia molesta</i>	425	12.46	Spherical	The phytoconstituents present in the leaf extract of aquatic fern involved in the bioreduction reaction and stabilizing the nanoparticles to produce stable NPs	Kumar et al. (2016a)
44	<i>Rauwolfia serpentina</i> Benth	427	7–10	Spherical	The phytoconstituents such as phenols, flavonoids, tannins, terpenoids, and proteins play a vital role in the reducing as well as capping during the stable synthesis of nanoparticles	Panja et al. (2016)
45	<i>Abutilon indicum</i>	455	5–25	Spherical	The phytochemical compounds such as polyphenols, flavonoids, alkaloids, and saponins in the leaf extract of <i>A. indicum</i> were responsible for the reduction reaction	Mata et al. (2015a)

(continued)

Table 6.1 (continued)

S. no.	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR	References
46	<i>Caesalpinia coriaria</i>	420	78 and 98	Triangle, hexagonal, and spherical	The phytochemical compounds like flavonoids, tannins, terpenoids, and polyphenols in the leaf extract are involved in the reduction reaction as well as stabilizing the metal ions during the synthesis of nanoparticles	Jeeva et al. (2014)
47	<i>Phoenix dactylifera</i>	439.5	30 and 85	Spherical	The functional groups of biomolecules in the <i>P. dactylifera</i> act as reducing agent for the formation of silver nanoparticles and capping agent during the synthesis of nanoparticles	Imtiaz et al. (2016)
48	<i>Santalum album</i>	423	80–200	Spherical and polydispersity	–	Swamy and Prasad (2012)
49	<i>Nicotiana tobaccum</i>	418	8	crystalline nature	Biomolecules and cell-metal ions interaction responsible for formation and stabilization of silver nanoparticles	Prasad et al. (2011)
50	<i>Solanum lycopersicum</i>	445	13	Spherical	–	Bhattacharyya et al. (2016)
51	<i>Trichodesma indicum</i>	445	20–50	Spherical with face centered cubic	–	Buhroo et al. (2017)

parts were responsible for the conversion of metal ions into nanoparticles (Prasad 2014). The characterization of the nanoparticles was done by UV, FTIR, XRD, SEM, and TEM analysis. The UV-visible spectral analysis was carried out in the synthesis of nanoparticles owing to its optical properties. By performing the UV-visible spectroscopy, the reduction of silver ions to silver nanoparticles was monitored (Ghaedi et al. 2015). The color change was ascribed to the excitation of the surface plasmon

Table 6.2 Fruit-mediated synthesis of silver nanoparticles

S. no	Plant name	UV-Visible (nm)	Size (nm)	Shape	FTIR analysis	References
1	<i>Cleome viscosa</i>	410–430	20–50	Spherical and irregular in shape	The phytochemicals (amino acids, alkaloids, phenol, carbohydrates, and tannins) act both reducing and capping agent	Lakshmanan et al. (2017)
2	<i>Emblica officinalis</i>	–	15	Spherical	The phytochemicals such as alkaloids, amino acids, tannins, and carbohydrates in the fruit extract were performed as reducing and stabilizing agent	Ramesh et al. (2015)
3	<i>Crataegus douglasii</i>	425–475	29.28	Spherical	–	Ghaffari-Moghaddam and Hadi-Dabanlou (2014)
4	<i>Piper longum</i>	430	46	Spherical	The phenolic constituents in the leaf extract of <i>P. longum</i> were involved in the capping and reduction reaction during the synthesis of nanoparticles	Reddy et al. (2014)
5	<i>Cassia fistula</i>	444.5–439.5	69	Spherical	The biomolecules in the fruit extract of <i>C. fistula</i> act as both reducing and stabilizing agent	Rashid et al. (2017)
6	<i>Momordica cymbalaria</i>	450	15.5	Spherical	The existence of several enzymes and phytochemicals in the fruit extract of <i>M. cymbalaria</i> was responsible for the reducing as well as capping agent during the synthesis of nanoparticles	Kumara et al. (2015)
7	<i>Carissa carandas</i> (Karonda) berry	420	10–60	Spherical	Carinol (and related resonant compounds) in the berry extract with inductive effect of the proton of methoxy and allyl groups, present at ortho and para positions of the compounds	Joshi et al. (2018)

resonance and the reduction of silver ions by the biomolecules present in the plant extract (Rasheed et al. 2017). The absorbance peak was formed due to the reduction of silver ions and characteristic of the SPR, thus indicating the formation of silver nanoparticles (Daisy and Saipriya 2012). The SEM, TEM, and XRD were used to

Table 6.3 Peel-mediated synthesis of silver nanoparticles

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
1	<i>Carica papaya</i>	400–435	16–20	Spherical	Phytochemicals and biomolecules such as proteins involved as both reducing and stabilizing agent	Balavijayalakshmi and Ramalakshmi (2017)
2	<i>Dragon fruit</i>	430–460	25–26	Spherical	The functional group such as carboxylic acid, phenol, alkanes, alkenes, and carbonyl group in the fruit peel might have been involved as stabilization and reduction agent for the formation of metal ions	Phongtongpasuk et al. (2016)
3	Mango	412–434	7–27	Spherical	The mango peel consists of carboxyl, hydroxyl, aldehydes, and ketones, which were involved in the reduction and stabilization of NPs	Yang and Li (2013)
4	<i>Citrus sinensis</i>	445–424	35 ± 2 and 10 ± 1	Spherical	The biomolecules present in the peel of <i>C. sinensis</i> act as a reducing and stabilizing agent for the synthesis of NPs	Kaviya et al. (2011)

determine the size, shape, and structure of the nanoparticles. The FTIR analysis was used to determine the functional groups present in the biomolecules. From the above Table 6.9, the highest size of the silver nanoparticles was synthesized by using the leaf of *Lantana camara* which ranges from 410 to 450 nm as well as the lowest size of the AgNPs was synthesized by the seed of *Prosopis farcta* (Patil Shrinivas and Kumbhar Subhash 2017; Miri et al. 2015). The phytochemicals present in the plants are the major sources responsible for the green synthesis of silver nanoparticles shown in Fig. 6.4. The antibacterial and antifungal activities of silver nanoparticles synthesized using different plants have been depicted in Tables 6.10 and 6.11, respectively.

The plant-mediated silver nanoparticles are widely used in various biomedical applications. Predominantly it plays an indispensable role in inhibiting the pathogenic bacteria. The antibacterial activity of silver nanoparticles was determined by performing the antimicrobial assay such as Kirby–Bauer method, minimum inhibitory concentration, and minimum bactericidal concentration. Commonly *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia*, *Streptococcus pneumonia*, and some other *Enterobacter* were inhibited by the synthesis of plant-mediated silver nanoparticles. Here are some of the illustrations given below about the AgNPs synthesized by the plants. The AgNPs synthesized by the fruit of *Cleome viscosa* have an ability to inhibit the gram-positive bacteria *S. aureus* and gram-negative bacteria like *E. coli* and *Klebsiella pneumonia*.

Table 6.4 Root-mediated synthesis of silver nanoparticles

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
1	<i>Dryopteris crassirhizoma</i>	–	5–60	Spherical	The functional groups (carboxyl, hydroxyl, alkyl, amide) and phytochemicals present in the rhizome may be used as a reducing and stabilizing agent for NPs	Lee et al. (2016)
2	<i>Coptis chinensis</i>	428	15–20	Spherical	The polyphenolic compounds present in the leaf extract especially chitosan act as capping and reducing agent	Ahmad et al. (2017)
3	<i>Bergenia ciliata</i>	425	35	Spherical	The phenolic compounds present in the rhizome part of plant might have been responsible for the reduction and stabilization of AgNPs	Phull et al. (2016)
4	<i>Diospyros paniculata</i>	428	14–28	Spherical	The biomolecules in the root extract act as a reducing agent in the synthesis of NPs	Rao et al. (2016)
5	<i>Acorus calamus</i>	421	31.83	Spherical	The presence of alcohol, phenol, carbonyl and aromatic amine in the rhizome extract plays a dual role in the reduction and stabilization of nanoparticles	Nakkala et al. (2014)
6	<i>Acorus calamus</i>	420	20–35	Spherical	The functional groups such as carboxylic, carbonyl, amino and hydroxyl groups in the rhizome extract were involved in the conversion of bio-reduction of metal ions to nanoparticles	Sudhakar et al. (2015)

It has been determined by the zone of inhibition present in the disc diffusion agar plate. The gram-positive bacteria exhibit the maximum zone of inhibition while comparing to gram-negative bacteria (Lakshmanan et al. 2017). By performing the MIC and MBC assays, it has been found that the AgNPs synthesized by the plant extract of *Aerva lanata* show the excellent antibacterial activity by inhibiting these pathogenic bacteria like *P. aeruginosa*, *E. coli*, *B. subtilis*, *S. aureus*, *E. faecalis*, *S. agalactiae*, and *Corynebacterium* (Appapalam and Panchamoorthy 2017). The good diffusion and minimum inhibitory concentration assays were performed to ascertain whether the AgNPs synthesized using the leaf extract of *Nigella arvensis* have an ability to inhibit the pathogenic bacteria. When compared to *P. aeruginosa* and *E. coli*, the *S. marcescens* shows highest ZOI (Chahardoli et al. 2018). The AgNPs synthesized by the bark extract of *Butea monosperma* exhibit highest antibacterial efficacy against *E. coli* and *B. subtilis* (Pattanayak et al. 2017). The agar diffusion method was performed to determine the antibacterial activity of the AgNPs prepared

Table 6.5 Whole plant-mediated synthesis of silver nanoparticles

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
1	<i>Aerva lanata</i>	300–700	50	Spherical	The presence of flavonoids, saponins, and polyphenols act as both reducing and stabilizing agent for the synthesis of silver NPs	Appapalam and Panchamoorthy (2017)
2	<i>Mentha piperita</i>	450	90	Spherical	The biomolecules present in the plant act as both reducing and stabilizing agent	Mubarakali et al. (2011)
3	<i>Dioscorea alata</i>	450	10–20	Spherical	The plant extract of <i>D. alata</i> consists of reducing and stabilizing agent property owing to the presence of biomolecules	Pugazhendhi et al. (2016)
4	<i>Vernonia cinerea</i> L.	426	40–75	Spherical	The biomolecules present in the plants act as a reducing and capping agent	Ramaswamy et al. (2015)
5	<i>Boerhavia diffusa</i>	418	25	Spherical	The presence of potent biomolecules in the plant extract act as reducing and stabilizing agent	Kumar et al. (2014)
6	<i>Cocos nucifera</i>	427–428	22	Spherical	The existence of phenolic compounds, terpenoids, and other aromatic compounds plays a vital role in the synthesis of AgNPs as reducing and stabilizing agent	Mariselvam et al. (2014)

(continued)

Table 6.5 (continued)

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
7	<i>Lippia nodiflora</i>	442	30–60	Spherical	The presence of phenolic compounds in the aerial parts of the plant was responsible for the silver nanoparticles reduction and stabilization.	Sudha et al. (2017)
8	<i>Artemisia tournefortiana</i>	420	22.89 ± 14.82	Spherical	The bioactive molecules of hydroxyl and carbonyl groups act as a reducing and stabilizing agent	Baghbani-arani et al. (2017)

Table 6.6 Bark-mediated synthesis of silver nanoparticles

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
1	<i>Butea monosperma</i>	424	35	Spherical	The phytochemicals present in the bark extract might act as a reducing and stabilizing agent	Pattanayak et al. (2017)
2	<i>Pongamia pinnata</i>	420	5–55	Spherical	The presence of phytochemicals such as piperine, phenolic amides, and some other reducing sugars are involved in the reduction and stabilization process	Rajeshkumar (2016a)
3	<i>Eucommia ulmoides</i>	413	5–14	Spherical	The potent bioactive molecules present in the bark extract act as a reducing agent as well as capping agent	Lü et al. (2017)
4	<i>Syzygium cumini</i>	427	20–60	Polydispersed		Prasad and Swamy (2013)

Table 6.7 Flower-mediated synthesis of silver nanoparticles

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
1	<i>Nyctanthes arbortristis</i>	–	5–20	Spherical and oval	The phytochemicals in the flower extract of <i>N. arbortristis</i> play a vital role in the synthesis of AgNPs as a potent bioreduction and stabilizing agent	Gogoi et al. (2015)
2	<i>Millettia pinnata</i>	438	49 ± 0.9	Spherical	The flower extract of <i>M. pinnata</i> has the ability to act as reducing and stabilizing agent	Rajakumar et al. (2017)
3	<i>Tagetes erecta</i>	430	10–90	Spherical, hexagonal, and irregular shape	The existence of phytochemicals such as flavonoids, saponins, phlobatannins, triterpenes, steroids, and tannins might have been involved in the synthesis of NPs in the form of reducing and capping agent	Padalia et al. (2015)
4	<i>Plumeria alba</i>	445	36.19	Spherical	The existence of phytoconstituents groups such as carboxylic, sulfhydryl, and amino act as both reducing and capping agent	Mata et al. (2015b)

Table 6.8 Stem-mediated synthesis of silver nanoparticles

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
1	<i>Garcinia mangostana</i>	430	30	Spherical in monodispersed nature	The biomolecules present in the stem extract act as a reducing agent	Karthiga (2017)
2	<i>Hibiscus cannabinus</i>	444	10	Spherical	The various carboxylic acids present in the <i>H. cannabinus</i> were involved in the reduction reaction to reduce the silver ion into silver nanoparticles	Bindhu et al. (2014)

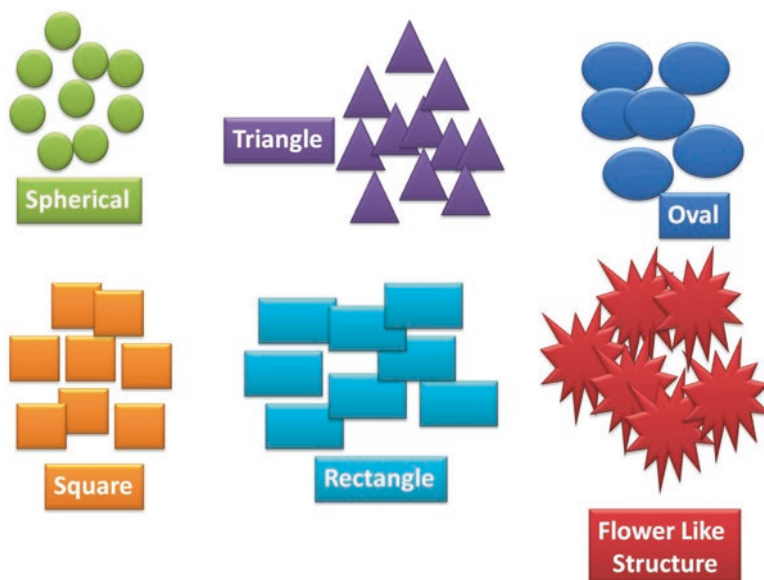
Table 6.9 Other parts of plant-mediated synthesis of silver nanoparticles

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
1	<i>Crocus sativus</i> L.	450	12–20	Spherical	The biomolecules such as flavonoids, phenols, glycosides, tannins, glycosides, terpenoids with carboxyl, ketone, aldehyde, and other functional groups play a vital role in reduction and stabilization	Bagherzade et al. (2017)
2	<i>Croton bonplandianum</i>	436 and 428	4–46	Spherical	The functional groups (hydroxyl, amino, amide, and carboxyl) of phytochemicals such as glucose, tannins, and proteins might have been involved in the reduction and stabilization process	Kumar et al. (2017a)
3	<i>Azadirachta indica</i> L.	418	<30	Spherical	The hydroxyl, carboxyl, and amino group present in the neem gum has a property of reducing and stabilizing the silver nanoparticles	Velusamy et al. (2015)
4	<i>Prosopis farcta</i>	433	8.5–11	Spherical	The biological molecule present in the extract plays a dual role in reducing as well as capping agent for the formation of NPs	Miri et al. (2015)
5	<i>Pistacia atlantica</i>	446	10–50	Spherical	The presence of amide groups in the protein plays an indispensable role in the capping of AgNPs	Sadeghi et al. (2015)

(continued)

Table 6.9 (continued)

S. no	Plant name	UV-visible (nm)	Size (nm)	Shape	FTIR analysis	References
6	<i>Watermelon</i>	425	109.97	Spherical	The existence of organic compounds such as flavonoids, lycopene, citrulline, and phenols in the rind of watermelon act as reducing and stabilizing agent for the formation of silver nanoparticles	Patra et al. (2016)
7	<i>Rosa indica</i>	441	23.52–60.83	Aggregated and spherical	The hydroxyl and amine groups of <i>R. indica</i> act as both reducing and stabilizing agent	(Ramar et al. 2015b)
8	<i>Coriandrum sativum</i>	421	13.09	Spherical, non-uniform and polydispersed	<i>Coriandrum sativum</i> acts as a capping agent	Nazeruddin et al. (2014)
9	Peanut	450	10–50	Spherical and oval	The phenolic, carboxylic, and amino groups in the peanut hull were responsible for the formation of silver nanoparticles	Velmurugan et al. (2015)

**Fig. 6.2** Different shapes of AgNPs synthesized by plant

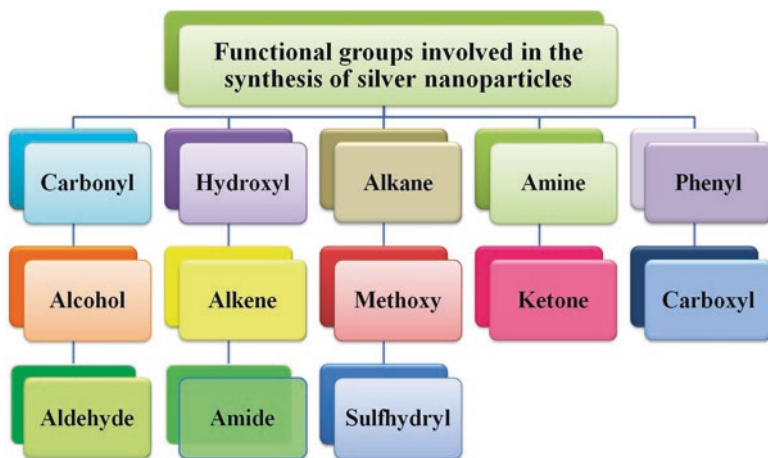


Fig. 6.3 Different functional groups involved in AgNPs synthesis

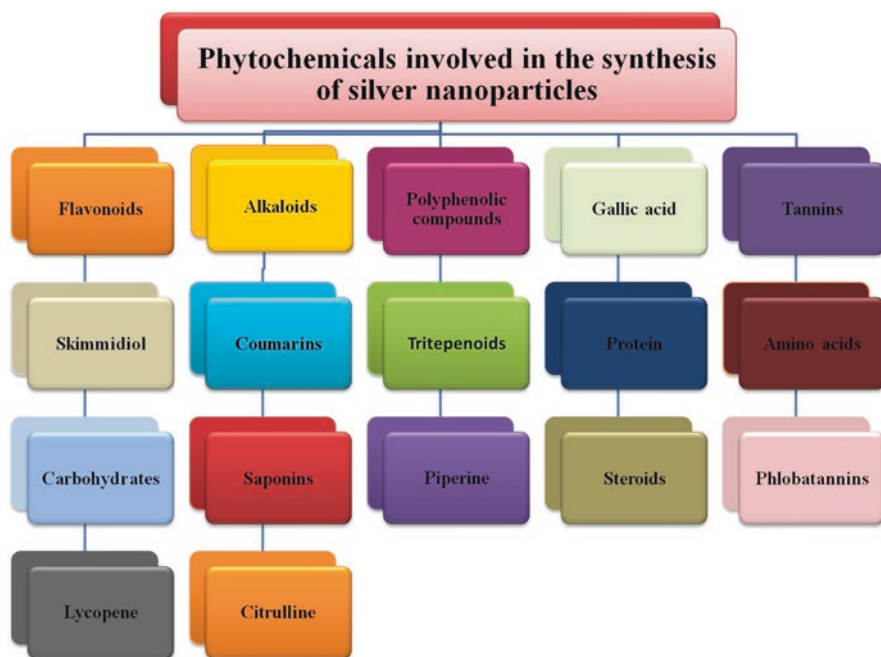


Fig. 6.4 Phytochemicals responsible for plant-mediated AgNPs

by the leaf of the *Skimmia laureola*. It has the capacity to inhibit the pathogenic bacteria like *S. aureus*, *K. pneumonia*, *P. aeruginosa*, and *E. coli* (Jamil et al. 2015). The MIC and MBC assays were carried out to find the antibacterial activity of the AgNPs prepared through the leaf extract of *Artemisia tournefortiana* (Baghbani-arani et al. 2017). The AgNPs callus and leaf extract of *Sesuvium portulacastrum* exhibit antibacterial activity against *S. aureus* and *Micrococcus luteus* (Sesuvium et al. 2010). The disc diffusion method was accomplished to identify the antibacterial activity of the leaf extract of *Artemisia vulgaris*. It has a potential to inhibit the organism like *E. coli*, *S. aureus*, *P. aeruginosa*, *Haemophilus influenza*, and *K. pneumonia* (Rasheed et al. 2017). It has been found that the AgNPs synthesized by the leaf extract of *Lantana camara* comprise antibacterial activity, antioxidant activity, and cytotoxicity (Patil Shrinivas and Kumbhar Subhash 2017). The AgNPs prepared by the flower extract of *Nyctanthes arbortristis* show potential antibacterial activity and cytotoxicity activities (Gogoi et al. 2015). The MIC determines the antibacterial activity of the AgNPs synthesized by the root extract of *Diospyros paniculata* (Rao et al. 2016).

The green synthesis of silver nanoparticles has an antifungal property. It inhibits against various fungal pathogens. Therefore, *Aspergillus* sp., *Penicillium* sp., *Candida* sp., and *Mucor* were most commonly inhibited by the silver nanoparticles. The assay like antimicrobial activity, minimum inhibitory concentration, and minimum bactericidal concentration were carried out to determine whether the fungi are inhibited by the silver nanoparticles. The penicillium was inhibited by the AgNPs synthesis by the leaf extract of *Phyllanthus amarus* (Ajitha et al. 2018). It inhibits by inactivating the sulfhydryl group present in the cell wall and lipids of fungi. By performing the disc diffusion method, it has been identified that the *Aspergillus fumigates*, *Fusarium solani*, *Aspergillus niger*, and *Aspergillus flavus* were inhibited by the AgNPs synthesized through the roots of *Bergenia ciliata* (Phull et al. 2016). The AgNPs synthesized by the root extract of *Diospyros paniculata* have an antibacterial activity. It inhibits against *P. notatum*, *A. flavus*, *S. cerevisiae*, *C. albicans*, and *A. niger* (Rao et al. 2016). The AgNPs produced by the hull of peanut exhibit highest antibacterial activity against *Phytophthora infestans* and *Phytophthora capsici* (Velmurugan et al. 2015).

6.2 Conclusion

This book chapter elucidates about the synthesis of silver nanoparticles using different parts of the plants like leaf, stem, flower, bark, roots, seed, peel, fruit, and aerial parts. It also explicates the phytochemicals and functional groups present in the plants. The plant-mediated synthesis of nanoparticles plays an indispensable role in the field of nanobiotechnology owing to its various applications like antifungal, antibacterial, antioxidant, cytotoxicity activities, and so on. Even though the green synthesis of nanoparticles has some limitations, it has been widely used nowadays when compared to a physical and chemical method of nanoparticle synthesis. From this review, it has been proved that the green synthesis of silver nanoparticles has an ability to inhibit most of the pathogenic bacteria and fungi.

Table 6.10 Antibacterial activity of plant-mediated synthesis of silver nanoparticles

S. no	Plant name	Parts	Bacteria	Remarks	References
1	<i>Phyllanthus amarus</i>	Leaf	<i>Pseudomonas</i>	Zone of inhibition = 11 mm	Ajitha et al. (2018)
2	<i>Cleome viscosa</i>	Fruit	<i>Staphylococcus aureus</i> , <i>E. coli</i> , <i>Klebsiella pneumonia</i>	Zone of inhibition against <i>S. aureus</i> —17 ± 0.8 mm <i>E. coli</i> —16 ± 0.8mm <i>K. pneumoniae</i> —14 ± 1.2 mm	Lakshmanan et al. (2017)
3	<i>Carica papaya</i>	Peel	<i>Escherichia coli</i> <i>Staphylococcus aureus</i>	Zone of inhibition against <i>E. coli</i> —75 mm <i>S. aureus</i> —65 mm	Balavijayalakshmi and Ramalakshmi (2017)
4	<i>Lippia nodiflora</i>	Aerial parts	<i>Streptococcus pneumonia</i> <i>E. coli</i>	Zone of inhibition against <i>S. pneumonia</i> —24.1 mm <i>E. coli</i> —22 mm	Sudha et al. (2017)
5	<i>Dryopteris crassirhizoma</i>	Rhizome	<i>Bacillus cereus</i> <i>Pseudomonas aeruginosa</i>	Well diffusion method	Lee et al. (2016)
6	<i>Aerva lanata</i>	Plant	<i>P. aeruginosa</i> , <i>E. coli</i> , <i>B. subtilis</i> , <i>S. aureus</i> , <i>E. faecalis</i> , <i>S. agalactiae</i> , and <i>Corynebacterium striatum</i>	Minimum inhibitory concentration and minimum bacterial concentration method	Appalam and Panchamoorthy (2017)
7	<i>Nigella arvensis</i>	Leaf	<i>Serratia marcescens</i> , <i>P. aeruginosa</i> , and <i>E. coli</i>	Well diffusion and MIC method Zone of inhibition against <i>S. marcescens</i> = 20 mm <i>P. aeruginosa</i> = 16 mm <i>E. coli</i> = 17 mm	Chahardoli et al. (2018)
8	<i>Melia azedarach</i> L.	Leaf	<i>E. coli</i> , <i>K. pneumonia</i> , <i>S. aureus</i> , <i>P. aeruginosa</i> , <i>Proteus</i> spp.	Paper diffusion method, Minimum inhibitory concentration (MIC)	Mehmood et al. (2017)
9	<i>Embllica officinalis</i>	Fruit	<i>E. coli</i> , <i>K. pneumonia</i> , <i>B. subtilis</i> , and <i>S. aureus</i>	Disc diffusion method	Ramesh et al. (2015)

(continued)

Table 6.10 (continued)

S. no	Plant name	Parts	Bacteria	Remarks	References
10	<i>Crocus sativus</i> L.	Aqueous extract of saffron	<i>E. coli</i> , <i>P. aeruginosa</i> , <i>K. pneumoniae</i> , <i>S. flexneri</i> , and <i>B. subtilis</i>	Minimum inhibitory concentration	Bagherzade et al. (2017)
11	<i>Butea monosperma</i>	Bark	<i>E. coli</i> <i>Bacillus subtilis</i>	Agar diffusion method Zone of inhibition against <i>E. coli</i> = 17 mm and <i>B. subtilis</i> = 16 mm	Pattanayak et al. (2017)
12	<i>Crataegus douglasii</i>	Fruit	<i>Staphylococcus aureus</i> <i>E. coli</i>	Disc diffusion method	Ghaffari-Moghaddam and Hadi-Dabanlou (2014)
13	<i>Calliandra haematocephala</i>	Leaf	<i>Escherichia coli</i>	Well diffusion method	Raja et al. (2017)
14	<i>Coptis chinensis</i>	Rhizome	<i>Escherichia coli</i> <i>Bacillus subtilis</i>	Agar well diffusion method Zone of inhibition against <i>E. coli</i> = 12 ± 1.2 mm <i>B. subtilis</i> = 18 ± 1.6 mm	Ahmad et al. (2017)
15	<i>Cassia roxburghii</i>	Leaf	<i>B. cereus</i> , <i>S. aureus</i> , <i>P. aeruginosa</i> , <i>E. coli</i>	Antimicrobial assay	Moteriya et al. (2017)
16	<i>Skimmia laureola</i>	Leaf	<i>S. aureus</i> , <i>K. pneumoniae</i> , <i>P. aeruginosa</i> , and <i>E. coli</i>	Agar diffusion method Zone of inhibition against <i>S. aureus</i> = 14.67 mm <i>K. pneumoniae</i> and <i>P. aeruginosa</i> = 14.33 mm <i>E. coli</i> = 11.67	Jamil et al. (2015)
17	<i>Artemisia tournefortiana</i>	Aerial parts	<i>Streptococcus pyogenes</i> , <i>P. aeruginosa</i> , and <i>B. subtilis</i>	Minimum inhibitory concentration and minimum bacterial concentration	Baghbani-arani et al. (2017)
18	<i>Mentha piperita</i>	Plant	<i>S. aureus</i> <i>E. coli</i>	Well diffusion method	Mubarakali et al. (2011)

S. no	Plant name	Parts	Bacteria	Remarks	References
19	<i>Dragon fruit</i>	Peel	<i>Escherichia coli, P. aeruginosa and S. aureus</i>	Disc diffusion assay Zone of inhibition against <i>E. coli</i> = 15 mm <i>P. aeruginosa</i> = 13 mm <i>S. aureus</i> = 14 mm	Phongtongpasak et al. (2016)
20	<i>Convolvulus arvensis</i>	Leaf	<i>E. coli</i>	Disc diffusion method and macro dilution method	Hamed et al. (2017)
21	<i>Ficus religiosa</i>	Leaf	<i>P. fluorescens, S. typhi, B. subtilis, and E. coli</i>	Kirby–Bauer disc diffusion method Zone of inhibition against <i>P. fluorescens</i> = 2.9 mm <i>S. typhi</i> = 2.9 mm <i>B. subtilis</i> = 2.8 mm <i>E. coli</i> = 2.7 mm	Nakkala et al. (2017)
22	<i>Pongamia pinnata</i>	Bark	<i>Klebsiella planticola and S. aureus</i>	Agar well diffusion method Zone of inhibition against <i>K. planticola</i> = 15 mm <i>S. aureus</i> = 13 mm	Rajeshkumar (2016b)
23	<i>Croton bonplandianum</i>	Aqueous extract of plant	<i>E. coli</i> <i>S. aureus</i>	Antimicrobial assay	Kumar et al. (2017a)
24	<i>Adathoda vasica</i>	Leaf	<i>Vibrio parahaemolyticus</i>	Agar bioassay and well diffusion method	Latha et al. (2016)
25	<i>Physalis angulata</i>	Leaf	<i>E. coli</i> <i>S. aureus</i>	Minimum inhibitory concentration	Kumar et al. (2017b)
26	<i>Lantana camara</i>	Leaf	<i>S. aureus</i> <i>P. aeruginosa</i> <i>E. coli</i>	Antibacterial assay Zone of inhibition against <i>S. aureus</i> = 28.1 mm <i>P. aeruginosa</i> = 21.3 mm <i>E. coli</i> = 22.1 mm	Patil Shrinivas and Kumbhar Subhash (2017)

(continued)

Table 6.10 (continued)

S. no	Plant name	Parts	Bacteria	Remarks	References
27	<i>Marsilea quadrifolia</i>	Leaf	<i>Escherichia coli</i>	Minimum inhibition concentration	Maji et al. (2017)
28	<i>Olive</i>	Leaf	<i>S. aureus</i> , <i>P. aeruginosa</i> , and <i>E. coli</i>	Well diffusion method	Khaili (2013)
29	<i>Eucommia ulmoides</i>	Bark	<i>S. aureus</i> <i>E. coli</i>	Paper disc diffusion method	Lü et al. (2017)
30	<i>Tinospora cordifolia</i>	Leaf	<i>Staphylococcus</i> sp. <i>Klebsiella</i> sp.	Zone of inhibition against <i>Staphylococcus</i> sp. = 13 mm <i>Klebsiella</i> sp. = 12.3 mm	Selvam et al. (2017)
31	<i>Andrographis echitoides</i>	Leaf	<i>Escherichia coli</i> <i>Staphylococcus aureus</i>	<i>E. coli</i> = 28 mm <i>S. aureus</i> = 23 mm	Elangovan et al. (2015)
32	<i>Mango</i>	Peel	<i>Escherichia coli</i> <i>Staphylococcus aureus</i> <i>Bacillus subtilis</i>	<i>E. coli</i> = 13 mm <i>S. aureus</i> = 14.5 mm <i>B. subtilis</i> = 11 mm	Yang and Li (2013)
33	<i>Citrus sinensis</i>	Peel	<i>E. coli</i> , <i>P. aeruginosa</i> and <i>S. aureus</i>	Agar well diffusion method	Kaviya et al. (2011)
34	<i>Sesuvium portulacastrum</i>	Callus and leaf	<i>S. aureus</i> and <i>Micrococcus luteus</i>	Zone of inhibition against <i>S. aureus</i> = 23 mm <i>M. luteus</i> = 8 mm	Sesuvium et al. (2010)
35	<i>Azadirachta indica</i> L.	Neem gum	<i>Salmonella enteritidis</i> and <i>Bacillus cereus</i>	Kirby–Bauer disc diffusion method	Velusamy et al. (2015)
36	<i>Prosopis farcta</i>	Seed	<i>S. aureus</i> , <i>B. subtilis</i> , <i>P. aeruginosa</i> , and <i>E. coli</i>	Disc diffusion method	Miri et al. (2015)
37	<i>Dioscorea alata</i>	Plant	<i>Staphylococcus auricularis</i> and <i>Escherichia coli</i>	Agar well diffusion assay	Pugazhendhi et al. (2016)
38	<i>Artemisia vulgaris</i>	Leaf	<i>E. coli</i> , <i>S. aureus</i> , <i>P. aeruginosa</i> , <i>Haemophilus influenzae</i> , and <i>K. pneumoniae</i>	Disc diffusion method	Rasheed et al. (2017)

S. no	Plant name	Parts	Bacteria	Remarks	References
39	<i>Ceropegia thwaitesii</i>	Leaf	<i>Salmonella typhi</i> and <i>Bacillus subtilis</i>	Disc diffusion method	Muthukrishnan et al. (2014)
40	<i>Solanum trilobatum</i>	Fruit	<i>Streptococcus mutans</i> , <i>enterococcus faecalis</i> , <i>E. coli</i> and <i>K. pneumonia</i>	Antibacterial assay	Ramar et al. (2015a)
41	<i>Lantana camara</i>	Leaf	<i>Pseudomonas</i> spp. and <i>Bacillus</i> spp.	Kirby–Bauer Disc diffusion method	Ajitha et al. (2015)
42	<i>Bryophyllum pinnatum</i>	Leaf	<i>E. coli</i> and <i>Bacillus megaterium</i>	MIC value for <i>E. coli</i> = 2.65 mm <i>B. megaterium</i> = 6.31 mm MBC value for <i>E. coli</i> = 5.98 mm <i>B. megaterium</i> = 8.34 mm	Kabir et al. (2017)
43	<i>Vernonia cinerea</i> L.	Whole plant	<i>S. aureus</i> <i>E. coli</i>	Disc diffusion method	Ramaswamy et al. (2015)
44	<i>Boerhaavia diffusa</i>	Plant	<i>Flavobacterium branchiophilum</i> , <i>A. hydrophila</i> , and <i>P. fluorescens</i>	MIC against <i>F. branchiophilum</i> -sensitive <i>A. hydrophila</i> -intermediate <i>P. fluorescens</i> -resistant Antibacterial activity <i>F. branchiophilum</i> = 15 mm <i>A. hydrophila</i> = 14 mm <i>P. fluorescens</i> = 12 mm	Kumar et al. (2014)
45	<i>Pistacia atlantica</i>	Seed	<i>S. aureus</i>	Antibacterial assay	Sadeghi et al. (2015)
46	<i>Bergenia ciliata</i>	Rhizome	<i>Micrococcus luteus</i> , <i>S. aureus</i> , <i>Bordetella bronchiseptica</i> , and <i>Enterobacter aerogenes</i>	Disc diffusion method	Phull et al. (2016)

(continued)

Table 6.10 (continued)

S. no	Plant name	Parts	Bacteria	Remarks	References
47	<i>Cocos nucifera</i>	Plant	<i>Klebsiella pneumoniae</i> , <i>Plesiomonas shigelloides</i> , <i>Vibrio alginolyticus</i> , and <i>Salmonella paratyphi</i>	Zone of inhibition against <i>K. pneumoniae</i> = 24 mm, <i>Plesiomonas shigelloides</i> = 21 mm, <i>V. alginolyticus</i> = 19 mm, and <i>S. paratyphi</i> = 16 mm	Mariselvam et al. (2014)
48	<i>Alternanthera dentata</i>	Leaf	<i>E. coli</i> , <i>P. aeruginosa</i> , <i>K. pneumoniae</i> , and <i>E. faecalis</i>	Disc diffusion method	Ashok et al. (2014)
49	<i>Crataegus douglasii</i>	Fruit	<i>E. coli</i> and <i>S. aureus</i>	Disc diffusion method	Ghaffari-Moghaddam and Hadi-Dabanlou (2014)
50	<i>Artocarpus altilis</i>	Leaf	<i>E. coli</i> , <i>P. aeruginosa</i> , and <i>S. aureus</i>	Kirby–Bauer disc diffusion method	Ravichandran et al. (2016)
51	<i>Mimusops elengi</i> L.	Leaf	<i>Klebsiella pneumoniae</i> , <i>Micrococcus luteus</i> , and <i>S. aureus</i>	Kirby–Bauer disc diffusion method Zone of inhibition against <i>K. pneumoniae</i> = 18 mm <i>M. luteus</i> = 10 mm <i>S. aureus</i> = 11 mm	Prakash et al. (2013)
52	Watermelon	Rind	<i>B. cereus</i> , <i>E. coli</i> , L. <i>monocytogenes</i> , <i>S. aureus</i> , and <i>S. typhimurium</i>	Antibacterial assay Zone of inhibition against <i>S. aureus</i> = 14.54 mm (highest activity) and L. monocytogenes = 9.12 mm (lowest activity) Minimum inhibitory concentration Minimum bactericidal concentration	Patra et al. (2016)
53	<i>Euphorbia hirta</i>	Leaf	<i>E. coli</i> and <i>S. aureus</i>	Antibacterial assay and minimum inhibitory concentration against <i>E. coli</i> and <i>S. aureus</i> (lowest concentration)	Kumar et al. (2017b)
54	<i>Nyctanthes arbortristis</i>	Flower	<i>Escherichia coli</i>	Agar well diffusion method	Gogoi et al. (2015)

S. no	Plant name	Parts	Bacteria	Remarks	References
55	<i>Milletia pinnata</i>	Flower	<i>E. coli</i> , <i>P. aeruginosa</i> , <i>Proteus vulgaris</i> , <i>S. aureus</i> , and <i>K. pneumonia</i>	Agar disc diffusion method <i>E. coli</i> = 20.25 ± 0.91 mm, <i>P. aeruginosa</i> = 17.13 ± 0.80 mm <i>Proteus vulgaris</i> = 0.64 ± 1.09 mm <i>S. aureus</i> = 15.09 ± 0.17 mm and <i>K. pneumonia</i> = 14.81 ± 0.34 mm Agar well diffusion method	Rajakumar et al. (2017)
56	<i>Ananas comosus</i>	Leaf	<i>S. aureus</i> , <i>S. pneumonia</i> , and <i>E. coli</i>	Agar well diffusion method	Elias et al. (2014)
57	<i>Acalypha indica</i>	Leaf	<i>E. coli</i> and <i>V. cholerae</i>	Minimal inhibitory concentration against <i>E. coli</i> and <i>V. cholerae</i> exhibited lowest concentration	Krishnaraj and Jagan (2010)
58	<i>Garcinia mangostana</i>	Stem	<i>E. coli</i> , <i>K. planticola</i> , and <i>B. subtilis</i>	Well diffusion method Contrast to <i>B. subtilis</i> , <i>E. coli</i> , and <i>K. planticola</i> exhibits highest zone of inhibition	Karthiga (2017)
59	<i>Sesbania grandiflora</i>	Leaf	<i>Pseudomonas</i> spp.	Kirby–Bauer disc diffusion method	Ajitha et al. (2016)
60	<i>Tagetes erecta</i> (marigold)	Flower	<i>E. coli</i> and <i>P. aeruginosa</i>	Synergistic antimicrobial activity	Padalia et al. (2015)
61	<i>Hemidesmus indicus</i>	Leaf	<i>S. sonnei</i>	Agar bioassay, well diffusion method and confocal laser scanning microscopic bacterial assay <i>S. sonnei</i> exhibits the highest zone of inhibition = 34 ± 0.2 mm	Latha et al. (2015)
62	<i>Diospyros paniculata</i>	Root	<i>B. subtilis</i> , <i>E. coli</i> , <i>P. aeruginosa</i> , <i>K. pneumonia</i> , <i>S. aureus</i> , <i>S. pyogenes</i> , <i>B. pumilus</i> , and <i>P. vulgaris</i>	MIC through microdilution broth method <i>B. subtilis</i> , <i>E. coli</i> , and <i>P. aeruginosa</i> show Maximum activity <i>K. pneumonia</i> , <i>S. aureus</i> , and <i>S. pyogenes</i> exhibit moderate activity Mild activity against <i>B. pumilus</i> and <i>P. vulgaris</i>	Rao et al. (2016)

(continued)

Table 6.10 (continued)

S. no	Plant name	Parts	Bacteria	Remarks	References
63	<i>Rosmarinus officinalis</i>	Leaf	<i>E. coli</i> , <i>P. aeruginosa</i> , <i>S. aureus</i> , and <i>B. subtilis</i>	Disc diffusion method	Ghaedi et al. (2015)
64	<i>Croton sparsiflorus morong</i>	Leaf	<i>S. aureus</i> , <i>E. coli</i> , and <i>B. subtilis</i>	Disc diffusion method	Kathiravan et al. (2015)
65	<i>Rosa indica</i>	Petal	<i>Streptococcus mutans</i> , <i>Enterococcus faecalis</i> , <i>E. coli</i> , <i>K. pneumoniae</i>	Agar well diffusion method	Ramar et al. (2015b)
66	<i>Prosopis farcta</i>	Leaf	<i>S. aureus</i> , <i>B. subtilis</i> , <i>E. coli</i> , and <i>P. aeruginosa</i>	Disc diffusion method	Miri et al. (2015)
67	<i>Atalantia monophylla</i>	Leaf	<i>S. aureus</i> , <i>B. cereus</i> , <i>K. pneumoniae</i> , and <i>E. coli</i>	Antimicrobial assay by disc diffusion method <i>S. aureus</i> = 37 mm and <i>B. cereus</i> = 36 mm shows maximum ZOI	Mahadevan et al. (2017)
68	<i>Ocimum tenuiflorum</i>	Leaf	<i>E. coli</i> , <i>C. bacterium</i> , and <i>B. subtilis</i>	Antimicrobial assay by disc diffusion method	Patil et al. (2012)
69	<i>Xanthium strumarium</i>	Leaf	<i>E. coli</i> and <i>S. aureus</i>	Disc diffusion assay	Kumar et al. (2016b)
70	<i>Coriandrum sativum</i>	Seed	<i>Bacillus subtilis</i>	Agar diffusion method	Nazeruddin et al. (2014)
71	<i>Mukia maderaspatana</i>	Leaf	<i>B. subtilis</i> , <i>K. pneumoniae</i> , <i>S. typhi</i> , and <i>S. aureus</i>	Disc diffusion assay	Harshiny et al. (2015)
72	<i>Cassia fistula</i>	Fruit	<i>E. coli</i> and <i>K. pneumoniae</i>	Minimum inhibitory concentration	Rashid et al. (2017)
73	<i>Acorus calamus</i>	Rhizome	<i>B. subtilis</i> , <i>B. cereus</i> , and <i>S. aureus</i>	Kirby-Bauer disc diffusion method	Nakkala et al. (2014)
74	<i>Plumeria alba</i>	Flower	<i>E. coli</i> and <i>B. subtilis</i>	Agar disc diffusion method Zone of inhibition against <i>E. coli</i> = 28 mm <i>B. subtilis</i> = 20 mm	Mata et al. (2015b)

Table 6.11 Antifungal activity of plant-mediated synthesis of silver nanoparticles

S. no	Plants name	Parts	Fungi	Remarks	References
1	<i>Phyllanthus amarus</i>	Leaf	<i>Penicillium</i>	The silver NPs have an ability to inactivate the sulfhydryl group present in the lipids and cell wall of fungi	Ajitha et al. (2018)
2	<i>Vernonia cinerea</i> L.	Plant	<i>Candida albicans</i> and <i>Penicillium notatum</i>	Antifungal susceptibility assay	Ramaswamy et al. (2015)
3	<i>Bergenia ciliata</i>	Rhizome	<i>Aspergillus fumigates</i> , <i>Fusarium solani</i> , <i>Aspergillus niger</i> , and <i>Aspergillus flavus</i>	Antifungal assay by disc diffusion method	Phull et al. (2016)
4	<i>Artocarpus altilis</i>	Leaf	<i>Aspergillus vesicolor</i>	Antimicrobial assay through disc diffusion method <i>A. vesicolor</i> shows minimal susceptibility	Ravichandran et al. (2016)
5	<i>Sesbania grandiflora</i>	Leaf	<i>Penicillium</i> spp.	Kirby–Bauer disc diffusion method	Ajitha et al. (2016)
6	<i>Tagetes erecta</i> (marigold)	Flower	<i>C. albicans</i> , <i>C. neoformans</i> , and <i>C. glabrata</i>	Synergistic antimicrobial activity <i>Candida albicans</i> shows maximum zone of inhibition compared to others	Padalia et al. (2015)
7	<i>Diospyros paniculata</i>	Root	<i>P. notatum</i> , <i>A. flavus</i> , <i>S. cerevisiae</i> , <i>C. albicans</i> , and <i>A. niger</i>	MIC through microdilution broth method <i>P. notatum</i> , <i>A. flavus</i> , and <i>S. cerevisiae</i> show maximum activity <i>C. albicans</i> and <i>A. niger</i> show moderate activity	Rao et al. (2016)
8	<i>Rosmarinus officinalis</i>	Leaf	<i>Aspergillus oryzae</i> and <i>C. albicans</i>	Disc diffusion method	Ghaedi et al. (2015)
9	<i>Croton sparsiflorus morong</i>	Leaf	<i>Mucor</i> sp., <i>Trichoderma</i> sp., and <i>Aspergillus niger</i>	Disc diffusion method	Kathiravan et al. (2015)
10	<i>Atalantia monophylla</i>	Leaf	<i>Candida albicans</i>	Antimicrobial assay by disc diffusion method <i>C. albicans</i> = 34 mm shows a minimum zone of inhibition MIC and MBC were also tested	Mahadevan et al. (2017)

(continued)

Table 6.11 (continued)

S. no	Plants name	Parts	Fungi	Remarks	References
11	<i>Rauvolfia serpentina Benth</i>	Leaf	<i>C. albicans</i> and <i>Aspergillus niger</i>	Agar well diffusion method	Panja et al. (2016)
12	<i>Peanut</i>	Shell	<i>Phytophthora infestans</i> and <i>Phytophthora capsici</i>	Zone of inhibition 5–6mm	Velmurugan et al. (2015)

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Chapter 7

Plants as Fabricators of Biogenic Platinum Nanoparticles: A Gambit Endeavour



Babita Jha, Anal K. Jha, and Kamal Prasad

7.1 Introduction

Nanotechnology unbolted fenestrations to “think big about small things” and demands daring manoeuvres on precipitous grounds. It not only controls and understands matter at length scales of 1–100 nm but also outright the expression of unique properties of nanomaterials due to small grain size as compared to bulk. The intensification in surface to volume ratio gives birth to active surfaces and discrete energy levels in nano-entities, which increase their probable applications in surface-based applications and electronic usage (Daniel and Astruc 2004). Moreover, advances in development of predefined nanostructures ensure its applicability and plays critical role in many key technologies leading to creation of novel class of nanomaterials. Nanostructured materials are the demand of time and have become the panacea to all present day issues leaving no person novice to it.

One of the blooming applications of nanotechnology is in the field of platinum group metals (PGMs) that include six metals, namely ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). Plethora of metallic nanoparticles have been fabricated and used in various applications but as far as PGMs are concerned the contributions are low and still in its blooming state (Fig. 7.1). These PGMs are in high demand but have low abundance in earth crust, thus making them valuable and expensive (Capeness et al. 2015). Platinum metal, one of the prime members of this group with its name derived from the Spanish word “platina” meaning “little silver”, is very scarce in nature around 0.01 ppm (Pedone et al. 2017). It is highly resistant to chemicals, exhibit excellent high-temperature features, has

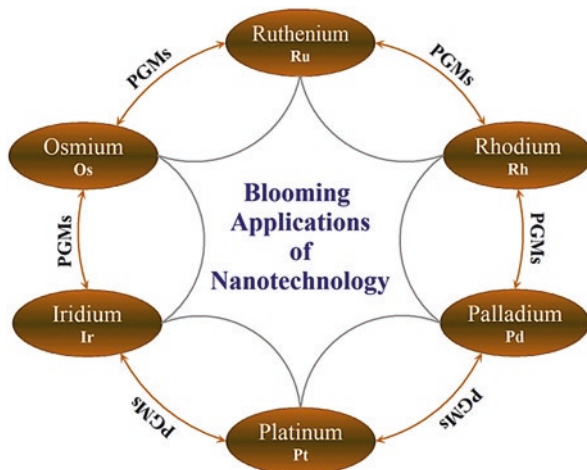
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Fig. 7.1 PGMs the field with blooming applications of nanotechnology



stable electrical properties, and is known for its catalytic properties since ages. With the growing needs of this rare and noble metal in so many sectors, nanotechnology has provided serviceability and platinum nanoparticles are all set to revolutionize the automotive sector (Golunski 2007; Yu et al. 2017), chemical industry (Du et al. 2015; Liu et al. 2015; Oberhauser et al. 2016; Zhang et al. 2016; Tatsumi et al. 2017; Li et al. 2017a, b; Yola and Atar 2017), and biomedical field (Asharani et al. 2010; Porcel et al. 2010; Liu et al. 2011; Manikandan et al. 2013; Shi et al. 2015).

The upraised demand due to widespread uses of platinum nanoparticles is alluring the nanotechnologists to provide possible solutions to its limited availability and look forth to its applicative potentials. Various fabrication routes for platinum nanoparticles are designed in order to give a replacement to bulk platinum metal. Catalysis which is the main essence of its applicability could be increased manifold when size is reduced to the nanoscale. The biomedical sector would be benefitted in diagnostic and treatment by optimization of its surface structure that determines the catalytic properties. This is a matter of attention and research, where new avenues are being deciphered, biosystems being of prime interest. The transitional hooks between the bulk and nanosized entities are ascertainable fabrication approaches, namely “bottom-up” and “top-down”. The “bottom-up” approach accredits that nano-entities “create themselves” by self-assembly of atom by atom, while “top-down” approach postulates splintering of larger entities to form nano-entities (Tiwari et al. 2008; Zhi and Müllen 2008; Merkel et al. 2010; Nugroho et al. 2016). Wherein each approach is brimming with their own advantages and disadvantages, herein, “bottom-up” approach as employed by biosystems with special reference to plants is discussed. This chapter summarizes the recent advances in the field of biogenic Pt NPs fabrication by plants and other biological sources and discusses the various mechanisms proposed behind it. It focuses on the possible benefits of employing plants in comparison to other biological sources.

7.2 Synthesis of Platinum Nanoparticles (Pt NPs)

Platinum nanoparticles owing to its best catalytic action have persuaded the designing of a variety of protocols for their synthesis. The nanoparticles are usually constructed by physical, biological, and chemical methods. The physical method proceeds by the “top-down” approach and the “bottom-up” approach is followed by chemical and biological methods as depicted in Fig. 7.2. These methods are focused to obtain desired physiochemical properties of the Pt NPs as these properties determine the appliance of these nanoparticles in various roles. In case of biomedical applications of Pt NPs besides its physiochemical properties its dispersion state and stability in biotic environment is a matter of contention (Moglianetti et al. 2016; Pedone et al. 2017). Biocompatibility of Pt NPs depends on size, symmetry; surface cladding and so are the synthetic ventures designed accordingly. Herein, we will precisely discuss the physical and chemical methods undertaken for fabrication of Pt NPs with desired characteristics along with its limitation. Then after, the main focus will be on the bioreductive synthesis of Pt NPs and plant in particular.

7.2.1 Physical Methods of Platinum Nanoparticles Fabrication

Physical methods of synthesis pursue the top-down approach and apply mechanism like mechanical pressure as in ball milling, chemical/thermal energy appliance for itching and electro-explosion, kinetic energy in sputtering, thermal energy in laser ablation, etc. to generate nanoparticles (Dhand et al. 2015). In the framework of Pt NPs, laser ablation techniques using laser beams in continuous or pulsed modes

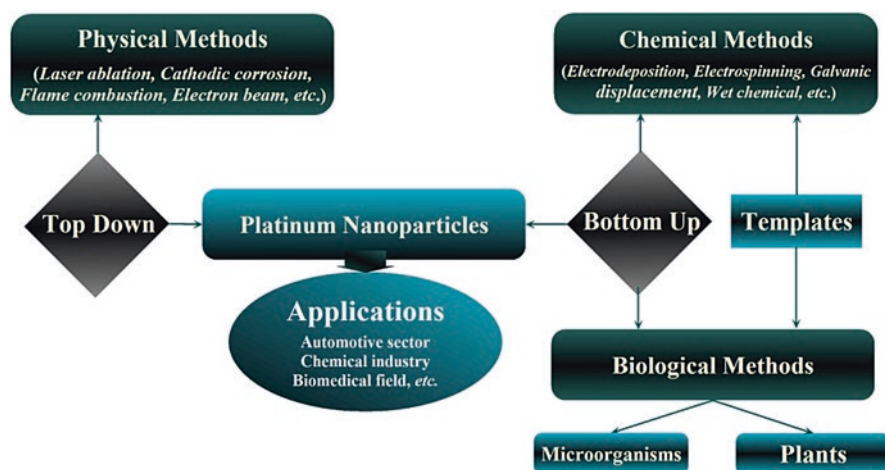


Fig. 7.2 Schematic representation of fabrication protocols of platinum nanoparticles

have been used to prepare platinum and its bimetallics with gold (Chau et al. 2011; Oko et al. 2015) tin (Bommersbach et al. 2008), thin films with cobalt (Rakshit et al. 2008), etc. This method helps to achieve Pt NPs of desired characteristics by varying the pulses, temperature, and other parameters. Aerosol-assisted vapour deposition has been employed to grow highly oriented nanoparticles of platinum (Paschos et al. 2008) and its deposition on tungsten trioxide nanowires (Annanouch et al. 2014). The fabrication of platinum by flame (Strobel and Pratsinis 2009; Choi et al. 2010), electron beam (Ke et al. 2013) and cathodic corrosion (Yanson et al. 2011) are also in practice. Cathodic corrosion method hinges on extreme cathodic polarization of a metal, which in turn produces cation-stabilized metal anions that act as precursors for genesis of nanoparticles. Physical methods bid adieu to the issues of solvent contamination and impurities caused by additives like stabilizer, surfactant as in chemical method. Yet there are limitations to the physical methods as shape and size tunability of nanoparticles is a tedious and difficult affair with resultant lesser yield (Kshirsagar et al. 2011). Besides it, in context of biomedical application their stability and behaviour in biological environment is a matter of research (Correard et al. 2014).

7.2.2 *Chemical Methods of Platinum Nanoparticles Fabrication*

Chemical synthesis of nanoparticles generally has the involvement of chemical agents like sodium borohydride (Jana et al. 2000), sodium citrate (Ranoszek-Soliwoda et al. 2017), *N,N*-dimethyl formamide (DMF) (Pastoriza-Santos and Liz-Marzán 2009; Zhang et al. 2014), ethyl alcohol (Liz-Marzán and Lado-Touriño 1996; Pal et al. 2009), cetyl trimethylammonium bromide (CTAB) (Moon et al. 2009; Vadivel et al. 2016), poly (*N*-vinyl pyrrolidone) (PVP) (Koczkur et al. 2015), etc. via the chemical reduction method (Bonnemann and Richards 2001). There are various attempts taken to synthesize Pt NPs of controlled shape and sizes via chemical methods (Ahmadi et al. 1996; Petroski et al. 1998; Wang et al. 2008; Leong et al. 2014) electrodeposition (Saminathan et al. 2009; Zhao et al. 2013), electrospinning (Kim et al. 2010), galvanic displacement (Mahmoud et al. 2010; Mahmoud and El-Sayed 2012), and electrochemical reduction (Mahima et al. 2008; Tiwari et al. 2009; Zhou et al. 2010; Li et al. 2012; Gao et al. 2013) are some of the examples. In context to platinum, wet chemical reduction has been reported to be the most powerful fabrication mechanism to generate shaped nanoparticles of required size distribution (Leong et al. 2014). Besides it, dendrimers have been engaged as templates in Pt NPs fabrication, favouring better control over the structure (Crooks et al. 1999; Yamamoto et al. 2009; Wang et al. 2013). These processes overall involve the usage of reducing agents to synthesize the nanoparticles by reduction of platinum salts. The initial platinum seed formation starts with nucleation followed by the growth stage that leads to the Pt NPs genesis. For desired characteristic Pt NPs synthesis,

various reducing agents, surfactants, organic acids, solvents, capping agents, etc. are employed; affecting the toxicological profile of the nanoparticles and thus limiting its uses. The large-scale production is also restrained because of the associated environmental issues.

7.2.3 Biological Methods of Platinum Nanoparticles Fabrication

The recent trends of nanoparticles fabrication pioneers the environmental friendly, biologically assisted synthesis processes wherein the biological organisms are employed to produce nontoxic, nano-entities in an easy and inexpensive way. The fabrication of Pt NPs by biological methods manifests to be superior to chemical and physical methods. Nanoscale processes and structures have been integral part of all the biosystems, being in charge of its viability and cognizance. The interaction between inorganic substances and biological entities has led to the focus on their potential applications for synthesis of nanomaterials and thus tempted their employment. These entities have been bestowed with the intrinsic properties to combat high concentration of toxic metal ions through distinct resistance mechanism. The detoxification action advances either by reduction/oxidation of metal ions or by the compilation of insoluble complexes. This very fact is the crux for assuming biological systems as the mantle of nanoparticle production. The organisms hired for the role as nano factories vary from simple prokaryotic cells to complex eukaryotic entities (Korbekandi et al. 2009).

With the advent of nanotechnology and explicitly nano-biotechnology, these biosystems have provided serviceability as factories for fabrication of novel functional nanoparticles and nanomaterials with diverse applications. Nano-biotechnological protocols agreeableness is on account of it being a simple, reliable, worthwhile, eco-friendly venture leading to synthesis of biocompatible nano-entities, unescorted by harmful chemicals. These protocols as a breakthrough in the nano ventures provided an alternative to physical and chemical methods of nanoparticle fabrication. There are ample of communications for bio-assisted syntheses of noble metals like silver and gold (Nadagouda and Varma 2006; Jha et al. 2008, 2009a; Jha and Prasad 2010, 2011a, b, 2013; Prasad et al. 2010; Mallikarjuna et al. 2011; Elia et al. 2014; Prasad 2014; Krithiga et al. 2015) as these are manufactured in a jiffy by even weak reducing agents. Bearing platinum in mind, there are only a few reports in literature describing the fabrication of platinum through the biological entities (Isaac et al. 2013; Siddiqi and Husen 2016; Whiteley et al. 2011). The overall fabrication of platinum nanoparticles can be roundly classified into three categories: Biogenic platinum by microorganisms, by proteins/enzymes/biomolecules as templates, and by plant/plant extracts.

7.2.3.1 Biogenic Platinum by Microorganisms

Microorganisms are endowed with remarkable capability to reduce the heavy metal ions to their respective highly stable nanoparticles with the aid of plethora of enzymes generated via their cellular machinery. It is a kind of defence mechanism to overcome metal toxicity and resultant are novel nanomaterials (Klaus-Joerger et al. 2001; Iravani 2014). The synthesis of nanoparticles by the microorganisms can be assorted into intracellular and extracellular banking upon the location of nanoparticle synthesis (Prasad et al. 2016). The intracellular process relies upon the transportation and enzymatic reduction of metal ions to generate nanoparticles inside the cell. While the extracellular process results in trapping of metal ions outside the cell and their gradual reduction by enzymes.

Bacteria prove to be an excellent source for synthesis of Pt NPs as they are easy to cultivate and manipulate. The first report of platinum fabrication by cyanobacterium, *Plectonema boryanum* UTEX 48 was conveyed by Lengke et al. about a decade ago in 2006. The reduction process was investigated for temperature gradient 25–100 °C. It was observed that by tweaking the incubation temperature and reaction times, the microbes can form nanostructures with distinct morphologies and crystallinity. Thirty to 300 nm nanoparticles were obtained in spherical and dendritic morphology (Lengke et al. 2006). Konishi et al. (2007) reported elemental platinum synthesis by *Shewanella algae* at neutral pH and temperature within 60 min on provision of lactate as the electron donor. Sulphate-reducing bacteria has been employed by researchers (Rashamuse and Whiteley 2007; Riddin et al. 2009) wherein platinum reduction comparative analysis between live cells, heat-killed cells, cell-free extract, and purified hydrogenase enzyme was done. Riddin et al. (2009) also deciphered the bioreductive mechanism of Pt(IV) to Pt(0) via Pt(II) through two different hydrogenase enzymes. The trend set by these initial works, lured many other researchers and diverse number of bacteria's were employed like Cyanobacteria (*Calothrix*, *Anabaena*) (Brayner et al. 2007), *Pseudomonas aeruginosa* SM1 (Srivastava and Constanti 2012), *Escherichia coli* (Attard et al. 2012; Bennett et al. 2012), *Acinetobacter calcoaceticus* (Gaidhani et al. 2014), *Desulfovibrio alaskensis* G20 (Capeness et al. 2015), *Streptomyces* sp. (Baskaran et al. 2017), and *Desulfovibrio vulgaris* (Martins et al. 2016). *Streptomyces* sp. generated nanoplatinum exhibited cytotoxicity against breast cancer cell lines, catalytic Pt NPs from *Desulfovibrio vulgaris* was used for removal of pharmaceutical compounds.

Fungus-mediated Pt NPs synthesis protocols have gained acceptance on account of it being eco-friendly, inexpensive, easily maintainable, easy to scale-up, quick reduction, and high yield of monodisperse nanoparticles secreted extracellularly (Rai et al. 2011; Whiteley et al. 2011; Kashyap et al. 2013; Soni and Prakash 2012; Honary et al. 2013; Quester, 2013; Yadav et al. 2015; Prasad et al. 2016). The primal report on use of *Fusarium oxysporum* f. sp. *lycopersici* for intercellular and extracellular platinum synthesis was given by Riddin et al. (2006). Varied shapes from hexagons, pentagons, squares, rectangles to circles of 10–100 nm varied size of nanoparticles were observed in micrographs. Extracellular 5–30 nm spherical Pt NPs have also been reported from *Fusarium oxysporum* (Syed and Ahmad 2012). Besides it,

Neurospora crassa and *Penicillium chrysogenum* have also been reported to fabricate Pt NPs (Castro-Longoria et al. 2012; Subramaniyan et al. 2018).

Reports on applicability of algae for platinum nanoparticle production are limited (Shiny et al. 2014, 2016). Seaweed *Padina gymnospora*, a brown alga, rich in sulphated polysaccharides, have been communicated for 5–20 nm sized spherical Pt NPs synthesis. These nanoparticles were assessed cytotoxicity against a 549 lung cancer cell lines. Thus, among the bountiful microbe's only exiguous bacteria, fungi, and algae are reported as bioreactors of platinum synthesis as laid out in Table 7.1.

7.2.3.2 Biogenic Platinum by Proteins/Enzymes/Biomolecules as Templates

The higher cost and immense use of Pt NPs act as an incentive for the researchers to develop unique and green methods of its synthesis. In this framework, several biogenic molecules, proteins, and enzymes were undertaken as templates for platinum synthesis. These macromolecules bioreductive mechanism also proved that removal of spatial constrictions of cells do not affect the potentiality of the cellular enzymes to reduce the respective salts to nanoparticles. Fungi *Fusarium oxysporum* was used for extraction of a cell-free, dimeric hydrogenase enzyme, that passively caused bioreduction of platinum salt (Govender et al. 2009, 2010). Consortium of sulphate-reducing bacteria was the organism of choice to investigate cell-free, cell-soluble protein extract for bioreductive process (Riddin et al. 2010). Apoferritin has also been reported for platinum nanoparticle fabrication (Deng et al. 2009; Fan et al. 2011). Besides it, glucose (Shin et al. 2009; Engelbrekt et al. 2010), antioxidant (gallic acid) (Ko et al. 2015), and vitamin B2 (riboflavin) (Nadaroglu et al. 2017) and bioreduction of Pt NPs have also been communicated. Other biogenic sources like honey (Venu et al. 2011) and egg yolk (Nadaroglu et al. 2017) have also been utilized for genesis of Pt NPs. Fabrication of Pt NPs through templates is guided by bottom-up approach and here lies a narrow articulation in between the chemical and biological methods. There are reports wherein such templates have been categorized under chemical methods. Herein, these templates with biological origins are summarized in Table 7.2.

7.2.3.3 Biogenic Platinum by Plant/Plant Extracts

Metal bioaccumulation in plants convened the ability of plants to reduce the metal ions, either at the site of access or at sites remote from ion penetrations. Further studies interestingly proved that the accumulated deposits were in form of nanoparticles (Makarov et al. 2014). These processes that are means to combat the adverse metal toxicity by plants provided an insight to the fact of using plants as tool for fabricator of various nanoparticles (Akhtar et al. 2013; Kharissova et al. 2013; Mittal et al. 2013; Makarov et al. 2014; Singh et al. 2016). There are reports wherein

Table 7.1 Biogenic platinum synthesized by microorganisms

S. no.	Source	Location	Size (in nm)	Morphology	References
Bacteria					
1	<i>Plectonema boryanum</i> UTEX 485	Intracellular and extracellular	30–300	Spherical, dendritic morphology	Lengke et al. (2006)
2.	<i>Shewanella algae</i>	Intracellular	5	–	Konishi et al. (2007)
3.	Sulphate-reducing Bacteria	Intracellular	–	–	Rashamuse and Whiteley (2007)
4.	Cyanobacteria (<i>Calothrix</i> , <i>Anabaena</i>)	Intracellular	3.2	–	Brayner et al. (2007)
5.	Sulphate-reducing bacteria	Intracellular	–	Amorphous	Riddin et al. (2009)
6.	<i>Pseudomonas aeruginosa</i>	Extracellular	450	Circular disks	Srivastava and Constanti (2012)
7.	<i>Escherichia coli</i> MC4100	Intracellular	2.3 (1% metal loading) 4.5 (20% metal loading)	Spherical	Attard et al. (2012)
8.	<i>Escherichia coli</i>	Intracellular	14	–	Bennett et al. (2012)
9.	<i>Acinetobacter calcoaceticus</i> PUCM1011	Intracellular	2–3	–	Gaidhani et al. (2014)
10.	<i>Desulfovibrio alaskensis</i> G20	Extracellular	–	–	Capeness et al. (2015)
11.	<i>Streptomyces</i> sp.	Extracellular	20–50	Spherical	Baskaran et al. (2017)
12.	<i>Desulfovibrio vulgaris</i>	Extracellular	–	–	Martins et al. (2016)
Fungi					
1.	<i>Fusarium oxysporum</i> f. Sp. <i>lycopersici</i>	Intracellular and extracellular	10–100	Hexagons, pentagons, circles, square, rectangles	Riddin et al. (2006)
2.	<i>Neurospora crassa</i>	Intracellular	4–35 20–110 17–76	Spherical single Pt NPs Spherical nanoaggregates Rounded nanoaggregates	Castro-Longoria et al. (2012)
3.	<i>Fusarium oxysporum</i>	Extracellular	5–30	Spherical	Syed and Ahmad (2012)

(continued)

Table 7.1 (continued)

S. no.	Source	Location	Size (in nm)	Morphology	References
4.	<i>Penicillium chrysogenum</i>	Extracellular	8.5 15	–	Subramaniam et al. (2018)
Algae					
1.	<i>Padina gymnospora</i>	–	5–20	Spherical	Shiny et al. (2014, 2016)

Table 7.2 Biogenic platinum synthesized by proteins/enzymes/biomolecules

S. no.	Source	Size (in nm)	Morphology	References
Protein/enzyme				
1.	Hydrogenase (<i>Fusarium oxysporum</i>)	100–140	Spherical	Govender et al. (2009)
2.	Horse spleen Apoferritin	4.7	Spherical	Deng et al. (2009)
3.	Protein extract (Sulphate-reducing Bacteria)	200–1000	Geometric with four straight edges Irregular	Riddin et al. (2010)
4.	Hydrogenase (<i>Fusarium oxysporum</i>)	30–40 40–60	Irregular Circular, triangular, pentagonal, hexagonal Nanoplates	Govender et al. (2010)
5.	Apoferritin	1–2	Spherical	Fan et al. (2011)
Biomolecules				
1.	Vitamin B2 (riboflavin)	9.7 8.4	Nanoparticles Nanowires	Nadagouda and Varma (2006)
2.	β -D-glucose	3.8	Nanoparticles Nanowires	Shin et al. (2009)
3.	Glucose	1.6–1.8	–	Engelbrekt et al. (2010)
4.	Antioxidant (Gallic acid)	22	–	Ko et al. (2015)
Other biogenic sources				
1.	Honey	2.2	Nanoparticles, nanowires	Venu et al. (2011)
2.	Egg yolk (quail egg)	7–50	Spherical	Nadaroglu et al. (2017)
3.	Bacterial cellulose matrix	3–4	Spherical	Yang et al. (2009)
4.	Bacterial cellulose matrix	6.3–9.3	Irregular	Aritonang et al. (2014)

whole plants like *Sinapis alba*, *Lepidium sativum*, and *Medicago sativa* have been studied for accumulation and translocation of Pt NPs within them (Bali et al. 2010; Asztemborska et al. 2015). The whole plant use for nanoparticles fabrication is limited up to detoxification or phytoremediation, as extraction and downstream processing is very cumbersome. The extraction and utilization of phyto-constituents, in the form of plant extracts for nanotransformation is easier, acceptable, and more in practice. With these views in mind, the penetration of biogenic synthesis in the

world of PGMs occurred, various plant/plant parts were then after explored for fabrication of nanoparticles, as depicted in Fig. 7.3.

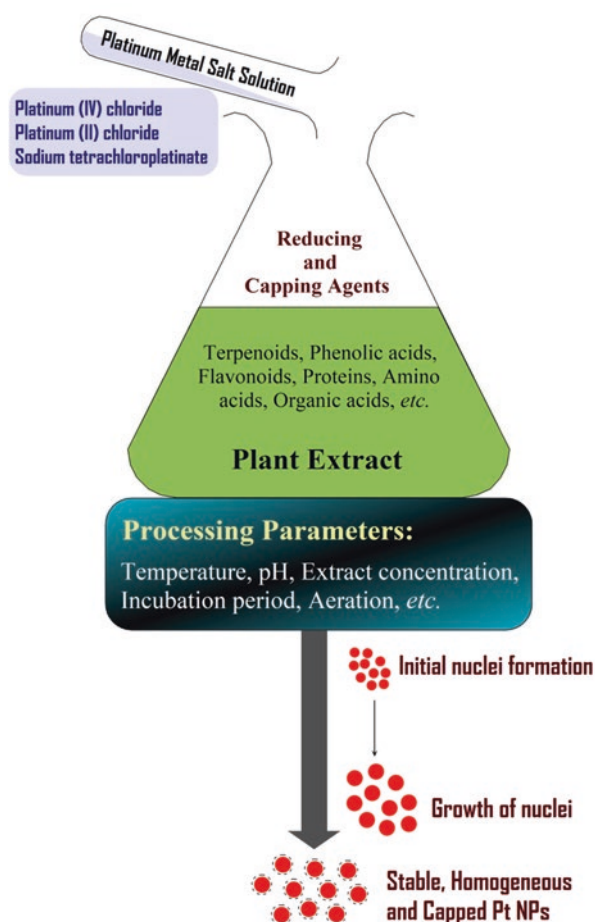
The generalized methodology adopted for Pt NPs fabrication involves the preparation of plant part extract either in aqueous or with other solvents. This extract is then charged with the platinum metal aqueous salt solution like platinum (IV) chloride, platinum (II) chloride, sodium tetrachloroplatinate, etc.; herein, the solubility of the Pt salt in water is an important factor. The processing parameters such as temperature, pH, extract concentration, incubation period, and aeration when properly maintained, the phyto-constituents acting as reducing and capping agents reacts with salt solution to give rise to initial Pt nuclei formation that with subsequent growth leads to stable, homogenous, and capped Pt NPs. General representation of the plant-mediated Pt NPs fabrication is depicted in Fig. 7.4.

The first report of extracellular fabrication of Pt NPs using leaf extracts of *Diospyros kaki* was reported by Song and his coworkers (2010). These researchers besides screening leaf extract as reducing agents for platinum fabrication also investigated the potential effect on the size of the synthesized particles with change in reaction conditions like temperature between 25 and 95 °C and varied concentrations of leaf broth and precursor platinum salt. The rate of Pt NPs synthesis increased with higher leaf broth concentration and increased in reaction temperature maximum being at 95 °C. The success story of this attempt was an initiative for latter works in this area, as tabulated in Table 7.3. Homogenous, highly stable, colloidal suspension of Pt NPs with size 2.4 nm was synthesized in aqueous medium using Gum exudates of Kondagogu tree (*Cochlospermum gossypium*) (Vinod et al. 2011). Soundarrajan et al. (2012) synthesized Pt NPs from *Ocimum sanctum* leaf extracts with conversion carried out at 100 °C, reduced Pt NPs were found as aggregates of irregular shape. The fabrication of palladium and platinum metal nanoparticles employing root extract of *Asparagus racemosus* at room temperature was reported wherein the metal salt platinum tetrachloride was reduced by the root extract and

Fig. 7.3 Plant parts used for platinum nanoparticle fabrication



Fig. 7.4 Plant-mediated fabrication of platinum nanoparticles



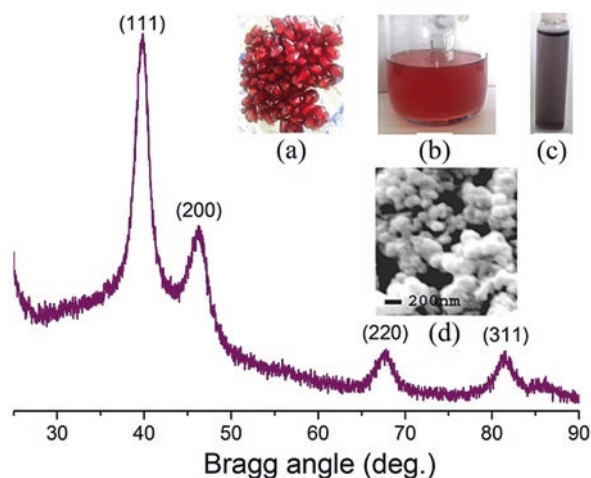
nanoparticles ranging in size between 1 and 6 nm were obtained within 5 min (Raut et al. 2013). *Cacumen platycladi* extract was used for bioreduction of sodium tetrachloroplatinate (Na_2PtCl_4) to Pt NPs and the variance that occurred in the flavonoid, reducing sugar and protein content of the plant extract was investigated (Zheng et al. 2013). Phytosynthesis of Pt NPs with restrained shape and dimensions has been reported by using plant wood nanomaterials (Lin et al. 2011). Isolated lignin from red pine (*Pinus resinosa*) has also served as a potent source for one-pot synthesis of Pt NPs (Coccia et al. 2012). Bimetallic heterogenous platinum-aurum of 10–40 nm size along with monogenous Pt NPs, 2–4 nm in size were fabricated using green tea (*Camellia sinensis*) and their photo-catalytic degradation of methylene blue was studied by Khalil (2016). With the advancement in this field various plant parts were taken in accord as leaves of *Anacardium occidentale* (Sheny et al. 2013), *Azadirachta indica* (Thirumurugan et al. 2016), *Mentha piperita* (Yang et al. 2017), Water hyacinth (John Leo and Oluwafemi 2017), *Withania somnifera* (Li

Table 7.3 Biogenic platinum synthesized by plant/plant parts

S. no.	Source	Parts used	Size (in nm)	Morphology	References
1.	<i>Diospyros kaki</i>	Leaves	2–12	Spheres Plates	Song et al. (2010)
2.	Hinoki timber	Wood flour	10	Spherical Cubic	Lin et al. (2011)
3.	<i>Cochlospermum gossypium</i>	Gum	2.4	–	Vinod et al. (2011)
4.	<i>Ocimum sanctum</i>	Leaves	23	Irregular	Soundarajan et al. (2012)
5.	<i>Pinus resinosa</i> (lignin and fulvic acid)	Wood	–	Irregular	Coccia et al. (2012)
6.	Beet	Root	<100	–	Kou and Varma (2012)
7.	<i>Asparagus racemosus</i>	Tubers	1–6	Spherical	Raut et al. (2013)
8.	<i>Anacardium occidentale</i>	Leaves	–	Irregular Rod shaped	Sheny et al. (2013)
9.	<i>Cacumen platycladi</i>	Plant biomass	2.4	–	Zheng et al. (2013)
10.	<i>Camellia sinensis</i>	Leaves	2–4	Spherical	Khalil (2016)
11.	<i>Punica granatum</i>	Peels	16–23	Spherical	Dauthal and Mukhopadhyay (2014)
12.	<i>Dioscorea bulbifera</i>	Tuber	2–5	–	Chopade et al. (2015)
13.	<i>Citrus sinensis</i>	Peels	23	Irregular	Castro et al. (2015)
14.	<i>Quercus glauca</i>	Leaves	5–15	Spherical	Karthik et al. (2016)
15.	<i>Fumariae herba</i>	Plant biomass	10–30	Pentagonal Hexagonal	Dobrucka (2016)
16.	<i>Alchornea laxiflora</i>	Bark	5.93	–	Olajire et al. (2017)
17.	<i>Taraxum laevigatum</i>	Plant biomass	2–7	Spherical	Tahir et al. (2017)
18.	<i>Azadirachta indica</i>	Leaves	5–50	Spherical	Thirumurugan et al. (2016)
19.	<i>Prunus × yedonis</i>	Gum	10–50	Spherical Oval	Velmurugan et al. (2016)
20.	<i>Mentha piperita</i>	Leaves	54.3	Spherical	Yang et al. (2017)
21.	<i>Punica granatum</i>	Peels	20.12	Spherical	Şahin et al. (2018)
22.	Water hyacinth	Leaves	3.74	Spherical	John Leo and Oluwafemi (2017)
23.	<i>Punica granatum</i>	Fruit	11	–	Jha et al. (2018)
24.	<i>Withania somnifera</i>	Leaves	12	Spherical	Li et al. (2017b)

et al. 2017a, b), besides it beet roots (Kou and Varma 2012), and fruit like *Punica granatum* (Jha et al. 2018) have been utilized. Jha et al. (2018) reported in the first hand the use of fruit part, arils of pomegranate for the fabrication of Pt NPs. The arils, extract prepared through it and the colloidal Pt NPs formed along with SEM image, are illustrated in the inset of Fig. 7.5a–d. The broadened XRD peaks clearly conveyed the formation of Pt NPs having face-centred cubic structure which are

Fig. 7.5 The arils (a), extract (b), and biosynthesized Pt NPs (c) with its X-ray diffraction pattern and SEM image (d) as fabricated by *Punica granatum*



semi-crystalline in nature with very small sized particles (~ nm) as depicted in X-ray diffraction pattern (Fig. 7.5) and SEM image.

The latitude of utilization of plants have been further intensified by using metabolite-rich agro-wastes like peels of pomegranate and orange (Dauthal and Mukhopadhyay 2014; Castro et al. 2015; Şahin et al. 2018) and plant biomass (Zheng et al. 2013; Tahir et al. 2017) for fabrication of this noble metal nanoparticles. The list in the Table 7.3 clearly gives an idea of the multiple numbers of plants utilized and diversification in the plant parts used for Pt NPs synthesis. This also revealed the success rate of fabrication by this approach and led to the need of deciphering the mechanistic aspect of these nanotransformations.

7.3 Mechanistic Aspect of Plant-Mediated Synthesis

Understanding the bioreductive mechanistic aspect underlying in the fabrication of Pt NPs is of core interest. Many researchers are emphasizing in this area although deciphered in chunks it largely remains unexplored. A generalized mechanism for fabrication of Pt NPs from plants is nearly impossible as phyto-constituents varies from plant to plant and the presence of variable phyto-composition among the plant parts makes it more complex. The contents of phytochemicals also fluctuate depending upon season, maturity, and geographical allocation of the plant concerned. The extracellular synthesis using plant extracts (Dauthal and Mukhopadhyay 2016) is more amenable as compared to whole plant usage; as this cocktail of complex structured compounds, with each performing different roles, work out synergistically as green chemical agents yielding the nanoparticles (Alam et al. 2013).

Song and his coworkers were the pioneers in the use of plants for Pt NPs fabrication. In their work using leaf extracts of *Diospyros kaki*, they discovered that for

conversion of >90% Pt NPs, 150 min was required at 95 °C as compared to 3 and 11 min when synthesizing silver and gold nanoparticles (Song et al. 2010). This relatively low rate was attributed to the difficulty in the initial nuclei formation that might be further linked to the higher positive electrochemical potential of Ag (0.80 V) and Au (1.0 V) as compared to Pt (0.74 V) (Haverkamp and Marshall 2009). The results of this study clearly suggested that fabrication of Pt NPs is not an enzyme-mediated process, as the rate of synthesis is greatest at 95 °C and no peaks associated with proteins/enzymes were obtained in FTIR. The functional groups attributed for Pt NPs fabrication included amines, ketones, aldehydes, alcohols, and carboxylic acids present in terpenoids and other reducing sugars. This fact that Pt NPs require higher temperature and longer reaction time was further supported by other researchers in their experiments with *Ocimum sanctum* (Soundarrajan et al. 2012), *Cacumen platycladi* (Zheng et al. 2013) to name a few. Carboxylic acid, phosphine, gallic acid, ascorbic acid, terpenoids, amines, and certain amino acids present in tulsi leaf extract acts as reducing agents for platinum ion reduction. In the fabrication of Pt NPs by tubers of *Asparagus racemosus* (Raut et al. 2013), various bioactive components like alkaloids, polysaccharides, steroids, terpenoids, coumarins, lactones, flavones, linalools, amino acids, and proteins were found to be involved as bioreducing agents in the reduction process at room temperature. Coccia et al. (2012) reported that the two aromatic naturally occurring derivatives of wood: Lignin and fulvic acid were involved in reduction of platinum metal ions in aqueous solution at 80 °C to the Pt NPs, as indicated by detection of vanillin and other low molecular weight derivatives in the reaction mixture. In another work by Lin et al. (2011), it is documented that wood nanomaterials besides acting as reducing agents also act as an excellent loading and stabilizing media. Zheng and coworkers fabricated Pt NPs with *Cacumen platycladi* extract and tried to explore the bioreductive mechanism underlying behind it. The content of reducing sugar, flavonoids, saccharides, and proteins were assessed before and after the reaction. A significant decrease in reducing sugar and flavonoids was seen as compared to the protein content that was indicative of their probable role in bioreductive process. The variation in these contents before and after the reaction; further varied by extract concentration, reaction temperature, and reaction time (Zheng et al. 2013). *Dioscorea bulbifera* tuber extract were reported to contain phytochemicals like saponins, ascorbic acids, citric acid, flavonoids, reducing sugars, and phenolics that play role in reduction and shape evolution of Pt NPs (Chopade et al. 2015). In neem leaf broth, terpenoids were believed to be the surface active molecules that besides stabilizing the nanoparticles also helped in its bioreduction (Thirumurugan et al. 2016). Castro et al. pointed on the fact that Pt system is more complicated as compared to Ag counterpart (Castro et al. 2015). They studied the effect of pH value of the medium on morphology control and valence state of precursor salt in the bioreduction process. The Pt NPs formed in acidic condition where irregular and encapsulated with Sulphur containing organic matter that helped in nanoparticle stabilization. This Sulphur was assumed to be of thiamine present in orange peel. At neutral pH, the shape was small and spherical and particle size and distribution tend towards more uniformity with increasing pH. In the fabrication of Pt NPs using pomegranate peels, Dauthal and

Mukhopadhyay (2014) explored the bioreduction mechanism. Phenolic hydroxyl groups present in polyphenolic compound, ellagic acid, and Pt^{4+} chelated to form an intermediate platinum complex. These phenolic hydroxyls were inductively oxidized to corresponding quinones. The Pt^{4+} to Pt^{2+} reduction occurred in the presence of free electrons or nascent hydrogen produced in the bioreduction process. The Pt^0 atoms further collided and Pt NPs formed, which was stabilized by quinones and ellagic acid. Thus, the bioreduction was attributed to polyphenolic compounds, ellagic acid, gallic acid, and quercetin. In case of Pt NPs fabrication by hot water extract of *Camellia sinensis* (green tea), FTIR analysis indicated polyphenols and caffeine as possible capping and stabilizing agents (Khalil 2016). The reduction and stabilization of Pt NPs by *Quercus glauca* aqueous leaves extract was attributed to functional groups such as flavonoids, carboxyl, tannins, amino, and glycosides or ether groups (Karthik et al. 2016). In the tree bark extract of *Alchornea laxiflora*, quercetin, has been identified as one of the important bioreducing agents along with proteins, polyols, and terpenoids helping in Pt NPs formation (Olajire et al. 2017).

The proposed mechanisms behind the fabrication of Pt NPs by plants are just reasonable hypotheses beyond authentic experimental basis. Further these hypotheses vary from plant to plant. Thus, as far as the specific mechanistic aspect is concerned it has not yet been interpreted well and requires in-depth evaluation. The huge and complex variety of phytochemicals present in various sources makes it challenging to identify specific reducing and stabilizing agents responsible for fabrication and stabilization of nanoparticles. In general, the bioreducing plant secondary metabolites that help in nanotransformation of Pt NPs can be broadly classified into flavonoids, polyphenols, terpenoids, proteins, and organic acids. The hydrogen and electron releasing potency of flavonoids are responsible for its reducing potentials (Zheng et al. 2013). Polyphenols usually form an intermediate complex due to metal chelating ability of its highly nucleophilic aromatic ring; this complex undergoes subsequent reduction to yield Pt NPs (Dauthal and Mukhopadhyay 2014). The hydroxyl group of terpenoids attributes it with reduction capabilities (Song et al. 2010; Raut et al. 2013; Shen et al. 2013). Proteins and amino acids are complex structured complexes with capability of bioreduction of Pt NPs (Raut et al. 2013). Organic acids like ascorbic acid and others have been reported for their role in nanoparticle fabrication in plant species from mesophytes, xerophytes, and hydrophytes genera (Jha et al. 2009a, b). These organic acids do act as reducing agents for Pt NPs fabrication in many plant species.

7.4 Conclusion

This chapter summarizes the recent research work in the fabrication of biogenic Pt NPs by conferring the various literatures reported so far. In the present scenario, wherein Pt NPs have wide implementation owing to its catalytic and medicinal properties, there is an urge for biological and environmental safety in their production. With increasing demand of precious Pt NPs, there was a need for a simple,

reliable, energy efficient, bio-compatible, cost-effective, and eco-friendly fabrication route for its synthesis. Pt NPs fabricated by physical and chemical methods suffered various disadvantages, green chemistry, and biological methods thus came into picture and have become the focal point of research. The fabrication of Pt NPs by plants emerged as advantageous competent to microbes with the presence of broad spectrum of phyto-constituents that act both as reducing and capping agents. Besides eliminating the elaborate process of nurturing cell cultures, the time span for Pt NPs synthesis by plants was much less than that by microorganisms like bacteria and fungi. Plant system can also be aptly scaled up for large-scale synthesis through tissue culture and optimization of downstream processing. In order to exploit and modify the fabrication route for optimized production of biogenic Pt NPs by plants, elucidation of the biochemical and molecular mechanistic aspect of the complete process is necessary. This would help in developing a rational approach and is pre-requisite in making this avenue economically competitive with the conventional methods. One aspect that was clear from this chapter is that mother nature has bestowed us with unique phytodiversity having immense possibilities thus dispensing “a challenging venture with rewarding results” for biogenic platinum nanoparticle fabrication.

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Chapter 8

Hidden Treasures for Nanomaterials Synthesis!



Niraj Kumari, Priti Kumari, Anal K. Jha, and Kamal Prasad

8.1 Introduction

Right from settlement of the mother earth, plant systems have played a crucial role in phylogenic diversity. The systematic origin of plant life has been evolved from aquatic system to top soil leading to formation of an adorable phytodiversity. The chemical constituents and metabolic promises decide the phylogenetic and functional fate of plants present in nature. Morphological organization, molecular distribution, and interaction of metabolites during metabolic fluxes (both primary as well as secondary) in plants contribute them with nature's blessing for adaptability and survival against different environmental harshness ranging from extremely cold alpine regions to deep ocean beds through deserts. Chemical constituents (or metabolic status) of plants provide strength for development of resistance against harsh environment and these chemical constituents also provide tremendous implications for surviving the humanity in nature. The interaction of inorganic nanoparticles with biological structures is one of the most promising areas of research in modern nanoscience and technology. The term nanotechnology is defined as the fabrications, manipulation, and utilization of materials at a scale smaller than 1 mm. The "nano" is a word which means dwarf or extremely small derived from a Greek word and used as prefix to any parameter. Physicist Professor Richard Feynman had given the concept of nanotechnology in his historic lecture "there's plenty of room at the bottom" in 1959 and the term was introduced by Professor Norio Taniguchi in Tokyo Science University in 1974. Nanoscience and technology is the area of research and

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development which deals with the development of synthesis methods and surface analytical tools for building structures and materials, as well as to understand the change in chemical and physical properties due to miniaturization, and also provides an opportunity of using such properties for the development of novel and functional materials and devices. Nanoparticles are described as particulate distribution of solid particles with at least one dimension of size range 10–1000 nm. The most important significance of nanoparticles is surface area to volume facet ratio which affirms to interact with other particles easier. There is alteration in the properties of conventional materials at nano level due to the quantum effect (spatial confinements); large surface area, large surface energy, and the behavior of surfaces start to lead the behavior of bulk materials. By amenably manipulating the structure, size, shape, and composition of the nanoscale materials, it is quite possible to tune their physical, chemical, electrical, optical, magnetic, mechanical, catalytic, and biological properties (Jha and Prasad 2011, 2014, 2016a, b, c; Vivek et al. 2012; Kaviya et al. 2011; Punuri et al. 2012; Venu et al. 2011; Daniel and Astruc 2004; Schmid 1992; Rastogi and Arunachalam 2013; Sen et al. 2013; Krishnaraj et al. 2012; Krolikowska et al. 2003; Valchev and Tosheva 2013; Gurunathan et al. 2009; Fayaz et al. 2011; Yilmaz et al. 2011; Castro et al. 2010; Pingali et al. 2005; Flores et al. 2013; Shin et al. 2004; Wang et al. 2007; Song and Kim 2009a, b; Kumar et al. 2012a, b, c, d, e, f; Jha et al. 2009a, b, c, d; Prasad et al. 2016). So the interface of nanotechnology in combination with biotechnology is arising to produce nanobiotechnology and its tremendous applications have been found in the field of medical science to engineering science and daily life. It is observed that there are several synthesis procedures for the preparation of ultrafine nanoparticles and few of them have been emerged with time. Generally there are two approaches involved in the syntheses of nanoparticles, a bottom-up approach (self-assembly) and a top-down approach. In bottom-up approaches, the nanoparticles can be synthesized by self-assembly of atom by atom, molecule by molecule and this is mostly depending on Gibbs free energy and/or follows the laws of thermodynamics, so that synthesized nanoparticles are in a state closure to a thermodynamic equilibrium state. In top-down approaches, nanoparticles can be synthesized by the use of conventional methods. A conventional method of nanosynthesis contains physical and chemical methods. So that nanosynthesis can be accomplished through several physical, chemical, biological, and amalgamated techniques (methods) such as extensive ball milling, mechanical grinding condensation or co-precipitation, sol-gel method, drawing glassy materials, biological fabrication and template based methods like materials around/within templates, etc. (Fig. 8.1). Synthesis of nanoparticles is one of the most important aims of nanotechnology with well-defined sizes, shapes, and controlled monodispersity. The most common method of nanosynthesis is physical and chemical methods; each of these methods synthesizes a mixture of nanoparticles with poor morphology which are either capital and/or labor, energy intensive, time consuming, employ hazardous chemicals such as strong reducing agents, polymer capping agents and surfactants, and also crave high temperature for reaction. The use of such toxic and perilous chemicals is responsible for various biological risks (Jia et al. 2009, Jha and Prasad 2010a, b, c; Chandran et al. 2006; Prasad 2014;

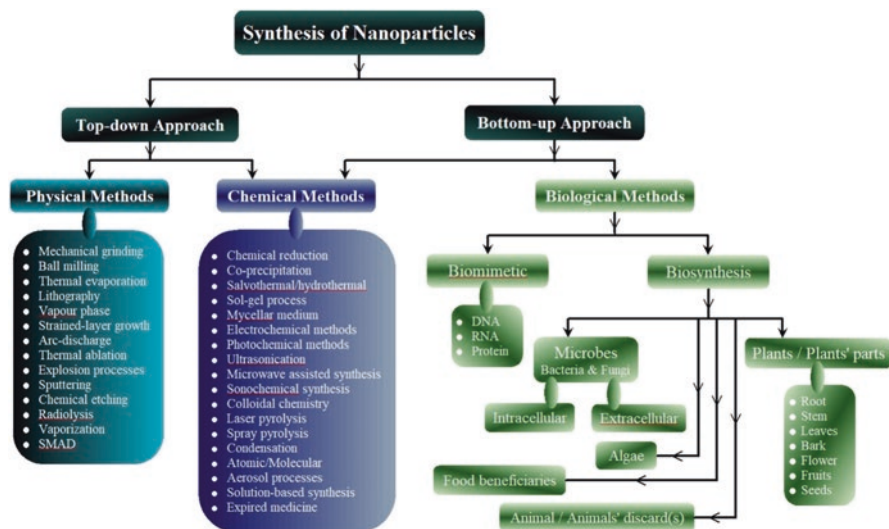


Fig. 8.1 Different synthetic routes for nanomaterials

Song et al. 2003, 2010; Xie et al. 2007; Sinha et al. 2009; Jha and Prasad 2011; Li et al. 2007; Kumar et al. 2011a, b, c; Prasad 2014; Prasad et al. 2016). Therefore, it is a demand of recent research approaches to develop a reliable, high yield, non-toxic, cost-effective, clean, less time consuming, eco-friendly method, which occurs at ambient conditions for the nanosynthesis. The biologically inspired nanosynthesis is evolving into an important branch of nanotechnology. Thus the biologically inspired nanosynthesis has been termed as biogenic synthesis/green synthesis/biological synthesis/biochemical synthesis/biomineralization in which a wide range of biological resources has been used for nanosynthesis like microorganisms (bacteria, yeast, fungi, algae, and viruses) (Prasad et al. 2016), plants, plant parts, animals, animal debris, expired medicine, etc. which studied under nanobiotechnology. The microbe-based protocols have been developed by several authors but the major drawback of microbe-based nanosynthesis is the obligatory constraint of aseptic conditions which requires longer time, trained staff, and the scaling-up cost. The plant-mediated nanosynthesis reduces the metal ions of corresponding nanoparticles in short time at low cost with easy availability of plant in nature which make them more preferred biological resources as compared to microbes. So the use of plant extracts for nanosynthesis is potentially advantageous which controls morphology and provides natural capping agents for the stabilization of nanoparticles. A lot of literature survey has been reported during the last two decades on plant-mediated nanosynthesis like silver, gold, platinum, iron, copper, copper oxide, zinc, zinc oxide, iron oxide, palladium, etc. because plant extracts have antioxidant or reducing properties which are responsible for them. In recent years, nanobiotechnology has originated as an upcoming field for the nanosynthesis. The growth of ecologically benign, “green” synthesis cues is in consonance with the recent RoHS

and WEEE legislation stipulated by the EU. It has been well known that living cells are the best examples of machines that operate at the nano level and perform a number of jobs ranging from generation of energy to extraction of targeted materials at very high efficiency. The ribosome, histone protein, DNA, chromatin, Golgi apparatus, interior structure of mitochondria, photosynthetic reaction center, and the fabulous ATPase are all nanostructures, which work quite efficiently. The cell factories have proved to be encouraging tools for the upcoming technologies and biomedical applications. Plant extracts have remarkable advantage in terms of metabolic flux (primary as well as secondary metabolites) which is good source of oxidizing/reducing agents for nanosynthesis (Leela and Vivekanandan 2008; Singh et al. 2011a, b; Jha and Prasad 2010b, 2012a, b, 2013; Agnihotri et al. 2009; Ahmad et al. 2002; Niraimathi et al. 2013; Kumar et al. 2008, 2012a, b, c, d, e, f; Song et al. 2009; Dubey et al. 2009; Dameron et al. 1989; Dameron and Winge 1990; Dean et al. 1997; Krishnamurthy et al. 2011; Prathna et al. 2011; Ahmad et al. 2003; Ankamwar et al. 2005; Fortin and Beveridge 2000; Ghosh et al. 2012a, b; Jha et al. 2008, 2009a; Krolkowska et al. 2003; Li et al. 1999; Philip 2009; Wang et al. 2009; Prasad and Jha 2009, 2010; Prasad 2014; Sanghi and Verma 2009; Saha et al. 2010; Zhu et al. 2011; Tripathy et al. 2010; Pandey et al. 2012; Jobitha et al. 2012; Karupiah and Rajmohan 2013; Ali 2011; Babu and Gunasekaran 2009; Marchiol 2012). This chapter will focus on how nature and material science can work together to create a “green” way of synthesizing metal/oxide/chalcogenide nanoparticles for a wide ambit of its application in different industries.

8.2 Bionanotechnology

Bionanotechnology is considered as one of the upcoming branches of nanotechnology in which biological sources can effectively be used for the synthesis of a plethora of nanoparticles of desired shape, size, and morphology. The nanosynthesis involving fabrication of different metal, oxide, or chalcogenide nanoparticles apparently this is the cumulative response of the biological system which being taken in to use and its immediate chemical ambience along with basic metabolic fluxes, metabolite content and signal transduction of the organism being engaged for the purpose. Plants are generally multicellular, eukaryotic, autotrophic organisms having cellulose containing cell walls and reproducing mostly sexually but asexual reproduction can also be common. Plants are characterized by the presence of green photosynthesizing unit chloroplasts. They have got naturally bestowed property to synthesize the complex molecules like carbohydrates, proteins, lipids as primary metabolites alkaloids, benzenoids, coumarins, flavonoids, lignans, lipid, sterol, tannins, triterpene, saponins, glycosides storage as secondary metabolites and these compounds are known to exhibit the physiological activities and medicinal properties (Tripathy et al. 2010; Bawankar et al. 2014; Ahmed and Hussain 2013; Salem et al. 2015; Premanathan et al.

2011; Prasad 2014; Azam et al. 2012; Gordon et al. 2011; Koli 2015; Namratha and Monica 2013). The mechanism of reduction of metals could be due to the conjugated oxidation-reduction reactions in which release of electrons are due to NADPH-dependent oxidoreductase. Most of the plant extract contain oxidoreductases, quinone, and anthraquinone which have played an important role in nanofabrication (Prasad et al. 2016). Presence of these metabolites in mostly all plant extract triggers a redox reaction due to tautomerization (keto to enol) leading to nanoparticles synthesis. The reduction of metal ions can also occur by means of the electrons carrier from NADPH to NADPH-dependent oxidoreductase. The oxidoreductases are pH sensitive and work in substitute manner. Oxidases get activated during lower value of pH, whereas reductases activated during higher value of pH. The expected mechanism for the synthesis of metal and metal oxide nanoparticles is illustrated in Fig. 8.2. The reduction potential of the plant broth seems to decide the fate of metal ions exposed. A high value of reduction potential at higher pH (>7) values is required for the formation of metal NPs while oxide NPs are resulted due to lower reduction potential at lower pH (< 7). The synthesis of plant-mediated metal/oxide nanoparticles and its conformation by different instruments are represented in form of flowchart in Fig. 8.3. It is well noted that pH value along with other parameters like kinetics, agitation rate, incubation time, temperature, reductant concentration, mixing ratio, and solution chemistry are deciding the moirai of metal ions to bio-reductant of plant extracts. So that protein has played an important role in the reduction of metal ions into its corresponding metal/oxide/chalcogenide nanoparticles and its stabilization. The formation of metal/oxide nanoparticles could be conformed using UV-Spectroscopy technique, afterwards these nanoparticles may be taken into use for further study (Shankar et al. 2004a, b; Kora et al. 2010; Jha and Prasad 2011, 2014, 2015, 2016a, b, c; Rao and Paria 2013).

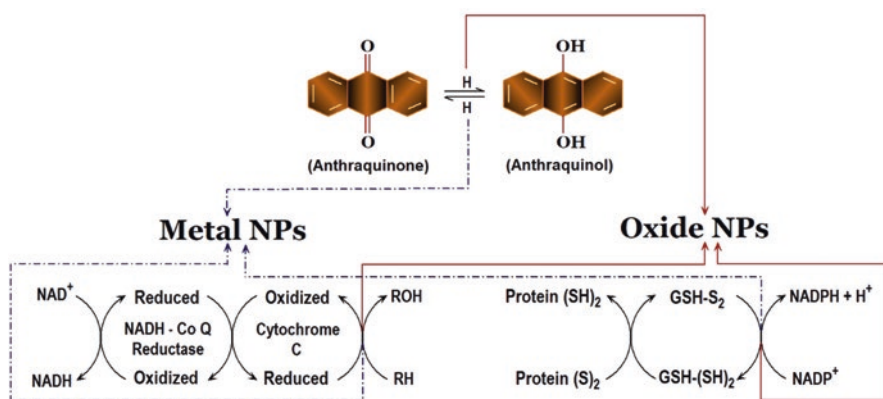
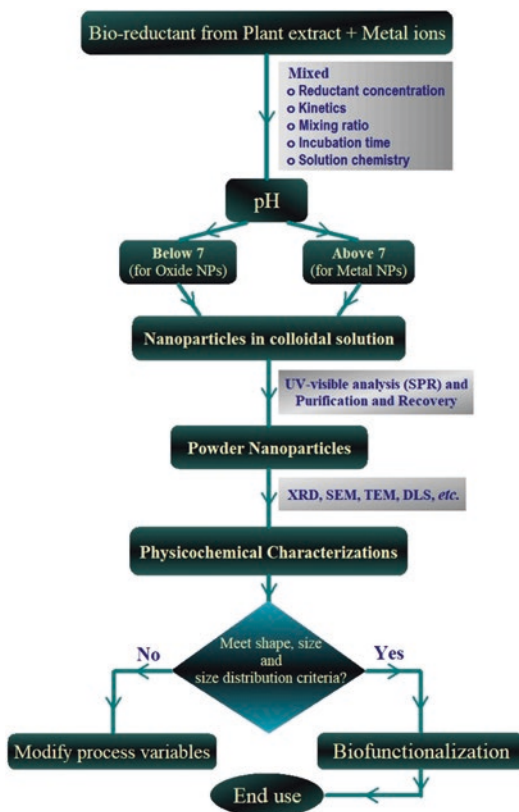


Fig. 8.2 Probable mechanism of plant-mediated nanosynthesis

Fig. 8.3 Flow diagram for the conformation of plant-mediated nanosynthesis



8.3 Methodology

A large number of plants have been described to facilitate nanosynthesis, which are discussed briefly in Table 8.1. The protocol of nanosyntheses involves: the collection of plant/plant parts from the available sites and washed thoroughly twice/thrice with tap water followed by distilled water to remove associated debris. Prior to the start of experiment, plant/plant parts like root, stem, bark, leaf, flower, fruit, seed, etc. was rinsed thoroughly by de-ionized water. Plant extract was prepared by taking defined amount (15 gm) of plant part thoroughly washed, dried, cut into fine pieces and mixed with 100 mL of 50% ethanol in a 250 mL conical flask and mixture was boiled for 20 min till the color changes from clear transparent to light green. The plant mass has been pressed by wrapping in serene cloth and 50 mL extract was collected under laminar flow which treated as source extract. A finite small portion of it (25 mL) was filtered and two times diluted by mixing distilled water. Now, 20 mL of 0.025(M) metal ion solution was mixed to the plant extracts solution. The mixed solution was heated on steam bath up to 60 °C for 10–20 min until appearance of deposition at the bottom of the flask, indicative of the inception of nano-transformation. Value of pH

Table 8.1 List of plant/plant parts used for biosynthesis of different nanoparticles

Plant	Plant parts	Nanoparticles	References
<i>Aegle marmelos</i>	Leaf	Ag	Jha and Prasad (2011)
<i>Annona squamosal</i>	Leaf	Ag	Song and Kim (2009a, b), Kumar et al. (2012a, b, c, d, e, f)
<i>Argemone mexicana</i>	Leaf	Ag	Singh et al. (2010a, b), Jha and Prasad (2014)
<i>Acalypha indica</i>	Leaf, seed, bark	Ag	Krishnaraj et al. (2010), Rao and Paria (2013)
<i>Alternanthera sessilis</i>	Leaf	Ag	Niraimathi et al. (2013)
<i>Andrographis paniculata</i>	Leaf	Ag	Suriyakalaa et al. (2013)
<i>Artemisia nilagirica</i>	Leaf	Ag	Song and Kim (2009a, b)
<i>Artemisia nilagirica</i>	Whole plant	Ag	Kumar et al. (2013a, b)
<i>Azolla</i> sp.	Leaf	Ag	Jha and Prasad (2016a, b, c)
<i>Azadirachta indica</i>	Leaf, seed, bark	Ag, Au, ZnO	Shankar et al. (2004a, b), Tripathy et al. (2010), Babu and Gunasekaran (2009), Ramezani et al. (2008), Thirumurugan et al. (2010), Bhuyan et al. (2015)
<i>Aegle marmelos</i>	Leaf	Au	Rao and Paria (2013)
Alfalfa	Leaf	Au	Montes et al. (2011)
<i>Ananas comosus</i>	Leaf	Au	Basavegowda et al. (2013)
<i>Allium sativum</i>	Bulb	Au	Rafiee et al. (2012)
<i>Allium cepa</i>	Bulb	Ag	Saxena et al. (2010)
<i>Achillea biebersteinii</i>	Leaf	Ag	Baharara et al. (2014, 2015)
<i>Arbutus Unedo</i>	Leaf	Ag	Kouvaris et al. (2012)
<i>Aloe vera</i>	Leaf	Ag, Au, Zn/ ZnO, Copper Oxide, In ₂ O ₃ , TiO ₂ , Fe, Mg doped ZnO	Chandran et al. (2006), Kathirvelu et al. (2009), Bhuyan et al. (2015), Maensiri et al. (2008), Medda et al. (2015), Muralikrishna et al. (2014), Kumar et al. (2015), Nithya et al. (2013), Rao et al. (2015), Yadav et al. (2016)
<i>Aloe barbadensis miller</i>	Leaf	Zn/ZnO	Sangeetha et al. (2011)
Banana	Peel	Au	Bankar et al. (2010a, b)
<i>Barbated Skullcup</i>	Leaf	Au	Wang et al. (2009)
<i>Benincasa hispida</i>	Seed	Au	Aromal and Philip (2012a, b)
<i>Beta vulgaris</i>	Sugar beet pulp	Au	Castro et al. (2011)
<i>Bryophyllum</i> sp.	Leaf	Ag	Jha et al. (2009a, b, c, d)
<i>Boswellia serrata</i>	Leaf	Ag	Kora et al. (2012)
<i>Brevibacterium casei</i>	Leaf	Ag	Kalishwaralal et al. (2010)

(continued)

Table 8.1 (continued)

Plant	Plant parts	Nanoparticles	References
<i>Boswellia ovalifoliolata</i>	Stem, bark	Ag	Savithramma et al. (2011)
<i>Basella alba</i>	Leaf	Ag	Leela and Vivekanandan (2008)
<i>Brevibacterium casei</i>	Leaf	Au	Yeary et al. (2005)
<i>Calotropis procera</i>	Leaf	Zn/ZnO	Singh et al. (2011a, b)
<i>Catharanthus roseus</i>	Leaf	TiO ₂	Velayutham et al. (2012)
<i>Cycas circinalis</i>	Leaf	Ag	Johnson and Prabu (2015), Ali (2011)
<i>Commelina benghalensis</i>	Leaf	Ag	Johnson and Prabu (2015)
<i>Citrus sinensis</i>	Peel	Ag	Konwarh et al. (2011), Zahir and Rahuman (2012)
<i>Citrus limon</i> (lemon)	Juice	Ag	Prathna et al. (2011)
<i>Cynodon dactylon</i>	Leaf	Ag	Sahu (2013)
<i>Cardiospermum halicacabum</i>	Leaf	Ag	Mitra (2012)
<i>Cinnamon zeylanicum</i>	Bark	Ag	Kumar et al. (2009a, b, c)
<i>Cycas</i>	Leaf	Ag	Jha and Prasad (2010a, b, c)
<i>Capsicum annum</i> L.	Fruit	Ag	Jha and Prasad (2011), Li et al. (2007)
<i>Carica papaya</i>	Fruit	Ag	Jha and Prasad (2015), Jain et al. (2009)
<i>Curcuma longa</i>	Tuber power	Ag	Kumar et al. (2011a, b, c)
<i>Cyperus</i> sp.	Leaf	Ag	Jha et al. (2009a, b, c, d)
<i>Coleus aromaticus</i>	Leaf	Ag	Vanaja and Annadurai (2013)
<i>Calotropis procera</i>	Leaf	Ag	Mohamed et al. (2014)
<i>Citrullus colocynthis</i>	Calli	Ag	Satyavani et al. (2011a, b)
<i>Clerodendron infortunatum</i>	Leaf	Ag	Jha and Prasad (2016a, b, c)
<i>Citrullus colocynthis</i>	Leaf	Ag	Satyavani et al. (2011a, b)
<i>Cassia auriculata</i>	Leaf	Ag	Udayasoorian et al. (2011)
<i>Cissus quadrangularis</i>	Leaf	Ag	Kumar et al. (2012a, b, c, d, e, f), Valli and Vaseeharan (2012)
<i>Camellia sinensis</i>	Leaf	Ag, ZnO	Nestor et al. (2008)
<i>Cocos nucifera</i>	Coir	Ag	Roopan et al. (2013)
<i>Cinnamomum camphora</i>	Bark, leaf	Ag	Huang et al. (2007)
<i>Catharanthus roseus</i>	Leaf	Ag	Kotakadi et al. (2013)
<i>Cochlospermum gossypium</i>	Leaf	Ag	Kora et al. (2010), Vinod et al. (2011)
<i>Coccinia grandis</i>	Leaf	Ag	Arunachalam et al. (2012)
<i>Chenopodium album</i>	Leaf	Ag	Dwivedi and Gopal (2010)
<i>Crossandra infundibuliformis</i>	Leaf	Ag	Kaviya et al. (2012)

(continued)

Table 8.1 (continued)

Plant	Plant parts	Nanoparticles	References
<i>Cymbopogon flexuosus</i>	Leaf	Au	Shankar et al. (2004a, b)
<i>Cicer arietinum</i>	Bean	Au	Ghule et al. (2006)
<i>Camellia sinensis</i>	Leaf	Au	Sharma et al. (2007)
<i>Coriandrum sativum</i>	Leaf	Au	Narayanan and Sakhivel (2008), Boruah et al. (2012)
<i>Cinnamomum zeylanicum</i>	Bark	Au	Smitha et al. (2009)
<i>Cuminum cyminum</i>	Seed	Au	Krishnamurthy et al. (2011)
<i>Cassia fistula</i>	Stem	Au	Daisy and Saipriya (2012)
<i>Cinnamomum camphora</i>	Whole plant	Au	Ahmad et al. (2003)
<i>Cochlospermum gossypium</i>	Leaf	Au, Pt	Agnihotri et al. (2009)
Cypress	Leaf	Au	Noruzi et al. (2012)
<i>Crocus sativus</i> (saffron)	Leaf	Au	Kumar et al. (2011a, b, c)
<i>Chenopodium album</i>	Leaf	Au	Satyavani et al. (2011a, b)
<i>Cassia auriculata</i>	Leaf	Au	Kumar et al. (2011a, b, c)
<i>Cacumen Platycladi</i>	Leaf	Au	Zhan et al. (2011)
<i>Carissa carandas</i>	Berries	Ag	Joshi et al. (2018)
<i>Centella asiatica</i>	Leaf	Au	Das et al. (2010)
<i>Calotropis procera</i> L.	Latex	Cu	Harne et al. (2012)
<i>Cinnamomum zeylanicum</i>	Bark	Pd	Kumar et al. (2009a, b, c)
<i>Curcuma longa</i>	Tuber	Pd	Kumar et al. (2009a, b, c)
<i>Cinnamomum camphora</i>	Leaf	Pd	Yang et al. (2010)
<i>Diospyros kaki</i>	Leaf	Pt	Song et al. (2010)
<i>Diospyros kaki</i>	Leaf	Ag	Song and Kim (2009a, b)
<i>Dillenia indica</i>	Fruit	Ag	Singh et al. (2013)
<i>Dioscorea bulbifera</i>	Tuber	Ag	Ghosh et al. (2012a, b)
<i>Dalbergia sissoo</i>	Leaf	Ag	Singh et al. (2012)
<i>Desmodium triflorum</i>	Leaf	Ag	Ahmad et al. (2011)
<i>Diospyrus kaki</i>	Leaf	Au	Song et al. (2009)
<i>Dalbergia sissoo</i>	Leaf	Au	Patil et al. (2012a, b)
<i>Eucalyptus camaldulensis</i>	Leaf	Au	Ramezani et al. (2008)
<i>Eclipta</i>	Leaf	Ag	Jha et al. (2009a, b, c, d)
<i>Eclipta prostrata</i>	Leaf	TiO ₂	Kumar et al. (2012a, b, c, d, e, f)

(continued)

Table 8.1 (continued)

Plant	Plant parts	Nanoparticles	References
<i>Euphorbia hirta</i>	Leaf	Ag	Elumalai et al. (2010), Priyadarshini et al. (2012)
<i>Eucalyptus</i> sp.	Leaf	Ag	Jha and Prasad (2012a, b)
<i>Euphorbia prostrata</i>	Leaf	Ag	Zahir and Rahuman (2012)
<i>Emblica officinalis</i>	Fruit	Ag, Au	Ankamwar et al. (2005), Jha et al. (2009a, b, c, d)
<i>Eucalyptus hybrida</i> (safeda)	Leaf	Ag	Dubey et al. (2009)
<i>Eclipta prostrate</i>	Leaf	Ag	Kumar and Rahuman (2011)
<i>Elettaria Cardamomum</i>	Leaf	Ag	Jobitha et al. (2012)
<i>Ficus amplissima</i>	Fruit, Flower	Ag	Johnson and Prabu (2015)
<i>Ficus benghalensis</i>	Fruit, Flower	Ag	Saxena et al. (2012)
<i>Ginkgo biloba</i>	Leaf	Ag	Song and Kim (2009a, b)
<i>Gelsemium sempervirens</i>	Leaf	Ag	Das et al. (2013a, b)
<i>Gracilaria corticata</i>	Leaf	Ag	Kumar et al. (2013a, b)
Guar gum	Latex	Au	Pandey et al. (2013)
<i>Gluconacetobacter xylinum</i>	Leaf	Iron/iron oxide	Zhu et al. (2011)
<i>Gardenia jasminoides</i>	Leaf	Pd	Jia et al. (2009)
<i>Glycine max</i>	Leaf	Pd	Petla et al. (2012)
Goat	Slaughter waste	ZnO	Jha and Prasad (2016a, b, c)
<i>Helianthus annuus</i>	Leaf	Ag	Leela and Vivekanandan (2008)
<i>Hydrilla</i> sp.	Whole plant	Ag	Jha et al. (2009a, b, c, d)
<i>Hydrastis canadensis</i>	Whole plant	Ag	Das et al. (2013a, b)
<i>Hevea brasiliensis</i>	Whole plant	Ag	Guidelli et al. (2011)
Henna	Whole plant	Ag, Au	Kasthuri et al. (2009), Banerjee and Narendhirakannan (2011)
<i>Hibiscus rosa sinensis</i>	Flower and leaf	Ag, Au	Singh et al. (2013)
<i>Hibiscus sabdariffa</i>	Leaf	ZnO	Bala et al. (2015)
Honey		Ag, Au, Pt	Kumar et al. (2009a, b, c), Philip (2009), Soundarrajan et al. (2012)
<i>Ixora coccinea</i>	Whole plant	Ag	Karuppiyah and Rajmohan (2013)
<i>Iresine herbstii</i>	Whole plant	Ag	Dipankar and Murugan (2012)
<i>Jatropha curcas</i>	Latex	Ag	Bar et al. (2009a)
<i>Jatropha curcas</i>	Seed	Ag	Bar et al. (2009b)

(continued)

Table 8.1 (continued)

Plant	Plant parts	Nanoparticles	References
<i>Justicia gendarussa burm</i>	Leaf	Au	Fazaludeen et al. (2012)
<i>Jatropha curcas</i>	Whole plant	TiO ₂	Hudlikar et al. (2012)
<i>Lippia nodiflora</i>	Whole plant	Ag	Johnson and Prabu (2015)
<i>Lippia citriodora</i>	Whole plant	Ag	Cruz et al. (2010)
Loquat	Whole plant	Ag	Awwad et al. (2013)
<i>Lonicera japonica</i> L.	Whole plant	Ag	Kumar and Yadav (2011)
<i>Lonicera japonica</i> L.	Whole plant	Au	Ali (2011)
Lemon grass (<i>Cymbopogon flexuosus</i>)	Juice	Au	Shankar et al. (2005), Singh et al. (2011a, b)
<i>Musa paradisiac</i>	Peeled banana	Pd	Bankar et al. (2010a, b)
Mangosteen	Whole plant	Ag	Veerasingam (2011)
<i>Mentha piperita</i>	Leaf	Au	Prasad and Jha (2009)
<i>Momordica charantia</i>	Whole plant	Au	Pandey et al. (2012)
<i>Moringa oleifera</i>	Whole plant	Ag	Prasad and Elumalai (2011), Mubayi et al. (2012)
<i>Magnolia Kobus</i>	Whole plant	Ag, Au	Song and Kim (2009a, b), Song et al. (2009)
<i>Mentha</i> sp.	Leaf	Ag	Jha and Prasad (2012a, b)
<i>Melia azedarach</i>	Whole plant	Ag	Sukirtha et al. (2012)
<i>Mukia scabrella</i>	Whole plant	Ag	Prabakar et al. (2013)
<i>Memecylon edule</i>	Whole plant	Ag, Au	Elavazhagan and Arunachalam (2011), Jha et al. (2007)
<i>Mentha piperita</i>	Whole plant	Ag	Ali et al. (2011)
<i>Murraya koenigii</i>	Leaf	Ag, Au, ZnO	Philip et al. (2011), Jha et al. (2009a, b, c, d), Divyapriya et al. (2014)
<i>Mangifera indica</i>	Leaf, fruit	Ag, Au	Phillip (2011), Phillip (2010)
<i>Mirabilis jalapa</i>	Flowers	Au	Vankar and Bajpai (2010)
<i>Manilkara zapota</i>	Leaf	Ag	Kumar and Rahuman (2012)
<i>Medicago sativa</i>	Seed	Ag	Lukman et al. (2011)
<i>Macrotyloma uniflorum</i>	Leaf	Ag, Au	Vidhu et al. (2011), Aromal et al. (2012)
<i>Malva parviflora</i>	Leaf	Ag	Zayed et al. (2012)
<i>Madhuca longifolia</i>	Leaf	Au	Sharma et al. (2007)
<i>Nicotiana tabacum</i>	Leaf	Ag	Prasad et al. (2011)
<i>Nyctanthes arbortristis</i>	Flower	Au	Das et al. (2011)
<i>Ocimum tenuiflorum</i>	Leaf	Ag	Patil et al. (2012a, b)
<i>Oryza sativa</i>		Ag	Leela and Vivekanandan (2008)
<i>Ocimum sanctum</i>	Root, stem	Ag	Ahmad et al. (2010a, b)

(continued)

Table 8.1 (continued)

Plant	Plant parts	Nanoparticles	References
<i>Ocimum basilicum</i>	Leaf	Au	Singhal et al. (2012)
<i>Ocimum</i> sp.	Leaf	Ag	Jha and Prasad (2012a, b)
Orange juice	Fruit	Ag, Zn/ZnO	Jha et al. (2011), Jha and Prasad (2015)
<i>Ocimum sanctum</i>	Leaf	Ag, Au, Pt	Singhal et al. (2011), Philip and Unni (2011), Rao et al. (2013), Mohamed et al. (2014), Soundarajan et al. (2012)
<i>Pelargonium, roseum</i>	Leaf	Au	Ramezani et al. (2008)
<i>Psidium guajava</i>	Leaf	Au	Raghunandan et al. (2010)
<i>Piper betle</i>	Leaf	Au	Punuri et al. (2012), Krishnamurthy et al. (2010)
<i>Punica granatum</i>	Peels	Au	Sharma and Singh (2013)
<i>Phyla nodiflora</i> Linn.	Whole plant		Sharma and Singh (2013)
<i>Panicum virgatum</i>	Leaf		Mason et al. (2012)
<i>Pelargonium graveolens</i>	Leaf	Ag, Au	Leela and Vivekanandan (2008), Shankar et al. (2003a, b)
<i>Pinus densiflora</i>	Leaf	Ag	Song and Kim (2009a, b)
<i>Platanus orientalis</i>	Leaf	Ag	Song and Kim (2009a, b)
<i>Piper betle</i>	Leaf	Ag	Mallikarjuna et al. (2012), Rani and Reddy (2011)
<i>Phytolacca decandra</i>	Leaf	Ag	Das et al. (2013a, b)
<i>Pergularia daemia</i>	Plant latex	Ag	Patil et al. (2012a, b)
<i>Papaver somniferum</i>	Leaf	Ag	Raghavan et al. (2012)
<i>Pithecellobium dulce</i>	Leaf	Ag	Raman et al. (2012)
<i>Punica granatum</i>	Peels	Ag, ZnO	Ahmad et al. (2012), Mishra and Sharma (2015)
<i>Piper betle</i> (Paan)	Leaf	Ag	Khan et al. (2012)
<i>Pandanus odorifer</i> (Forssk.)	Leaf	Ag	Panda et al. (2011)
<i>Pinus resinosa</i>	Bark	Pd, Pt	Coccia et al. (2012), Ingle et al. (2009)
<i>Parthenium hysterophorus</i>	Leaf	Zn/ZnO	Rajiv et al. (2013), Sindhura et al. (2014)
<i>Polygala tenuifolia</i>	Leaf	Zn/ZnO	Nagajyothi et al. (2015)
Rice husk	Dry powder	SiO ₂	Rafiee et al. (2012)
<i>Rosa</i> sp.	Leaf, flower	Ag	Jha and Prasad (2013)
<i>Rosa damascene</i>	Leaf, flower	Ag, Au	Ghoreishi et al. (2011), Shankar et al. (2003a, b)
<i>Rhizophora mucronata</i>	Leaf	Ag	Umashankari et al. (2012)
<i>Rosa hybrid</i>	Petal	Au	Noruzi et al. (2011)
<i>Syzygium aromaticum</i>	Whole plant	Au	Deshpande et al. (2010)
<i>Santalum album</i>	Leaf	Ag	Swamy and Prasad (2012)

(continued)

Table 8.1 (continued)

Plant	Plant parts	Nanoparticles	References
<i>Stevia rebaudiana</i>	Whole plant	Au	Mishra et al. (2010)
<i>Sphearanthus amaranthoids</i>	Whole plant	Au	Nellore et al. (2012)
<i>Sorbus aucuparia</i>	Whole plant	Au	Phillip (2011)
<i>S. torvum</i> (Solanaceae)	Whole plant	Au	Govindaraju et al. (2011)
<i>Saccharum officinarum</i>	Whole plant	Ag	Leela and Vivekanandan (2008)
<i>Sorghum bicolor</i> Zea mays	Seed	Ag	Leela and Vivekanandan (2008)
<i>Syzygium cumini</i>	Whole plant	Ag	Kumar et al. (2010a, b), Kumar and Yadav (2012)
<i>Syzygium cumini</i>	Seed	Ag	Kumar et al. (2010a, b)
<i>Syzygium cumini</i>	Seed	Ag	Banerjee and Narendhirakannan (2011)
<i>Syzygium cumini</i>	Leaf	Ag	Prasad et al. (2012)
<i>Syzygium cumini</i>	Bark	Ag	Prasad and Swamy (2013)
<i>Svensonia hyderabadensis</i>	Whole plant	Ag	Rao and Savithramma (2011)
<i>Shorea tumbuggaia</i>	Stem bark	Ag	Savithramma et al. (2011)
<i>Solanum lycopersicum</i>	Fruit	Ag	Bhattacharyya et al. (2016)
<i>Sorghum</i> spp.	Bran powder	Ag	Njagi et al. (2010)
<i>Spirulina platensis</i>	Whole plant	Ag	Mahdieh et al. (2012)
<i>Sesbania grandiflora</i>	Whole plant	Ag	Das et al. (2010)
<i>Sesuvium portulacastrum</i> L.	Whole plant	Ag	Nabikhan et al. (2010)
<i>Sorbus aucuparia</i>	Whole plant	Ag	Dubey et al. (2010a, b)
<i>Solanum nigrum</i>	Whole plant	Zn/ZnO	Ramesh et al. (2015)
<i>Sorghum</i> spp.	Bran powder	Iron/iron oxide	Njagi et al. (2011)
<i>Tanacetum vulgare</i>	Fruit	Au	Jha et al. (2009a, b, c, d)
<i>Terminalia catappa</i>	Leaf	Au	Ankamwar (2010)
<i>Trigonella foneugraecum</i>	Leaf	Au	Aromal and Philip (2012a, b)
<i>Terminalia chebula</i>	Leaf	Au	Kumar et al. (2012a, b, c, d, e, f)
Tea polyphenols	Leaf	Ag	Moulton et al. (2010)
<i>Tinospora cordifolia</i>	Leaf	Ag	Jayaseelan et al. (2011)
<i>Thuja occidentalis</i>	Leaf	Ag	Das et al. (2013a, b)
<i>Tanacetum vulgare</i>	Fruit	Ag	Kumar et al. (2012a, b, c, d, e, f)
<i>Terminalia chebula</i>	Leaf	Ag	Dubey et al. (2010a, b)
<i>Trachyspermum ammi</i>	Leaf	Ag	Raghavan et al. (2012)

(continued)

Table 8.1 (continued)

Plant	Plant parts	Nanoparticles	References
<i>Trichodesma indicum</i>	Leaf	Ag	Buhroo et al. (2017)
<i>Trianthema decandra</i>	Leaf	Ag	Geethalakshmi and Sarada (2010)
<i>Tribulus terrestris</i> L.	Fruit	Ag	Gopinath et al. (2012)
<i>Withania somnifera</i>	Leaf	Ag	Nagati et al. (2012)
Wood	Stem	Pt	Lin et al. (2011)
<i>Zingiber officinale</i> rhizome	Leaf	Ag	Kumar et al. (2012a, b, c, d, e, f)
<i>Zingiber officinale</i>	Leaf	Ag	Kumar et al. (2012a, b, c, d, e, f), Singh et al. (2010a, b)
<i>Zingiber officinale</i>	Leaf	Au	Jha and Prasad (2010a, b, c), Kumar et al. (2011a, b, c)

of the mixed plant extract solution is suitably adjusted at this stage depending upon targeted task synthesis of a metal or an oxide or chalcogenide. It is allowed to cool further in the laboratory ambience. After overnight, the mixed plant extract solution is noticed to have distinctly marked deposits. It is filtered through a Whatman filter paper and dried for subsequent characterization. The syntheses of nanoparticles were checked by UV-visible spectroscopy.

8.4 Conclusion

This chapter encompasses the various methods for nanoparticle synthesis and with changing pace of time the demand of nanoparticles in different fields is bound to rise so this can very well be met by going for green options like plant based synthesis. These natural plants are wonderful amenable resource for nanofabrication with less time consuming, eco-friendly, nontoxic, and easy protocols for scaling up. Hence, this green synthesis of nanoparticles will result in a significant payoff for the field of medical science.

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Chapter 9

Synthesis of Functionalized Nanoparticles for Biomedical Applications



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9.1 Introduction

History of nanoscience and technology can be traced back to the ancient Indian and Greek literatures. Ever inquisitive nature of the human beings might have led to the exploration and establishment of a plant as a source of medicine. The time changed its face and observations got transcribed in meticulous inscriptions and consequently translated into applications. Charak and Sushruta Samhita are the two such examples from our ancient literatures. Especially, Charak Samhita, Ras ratnakar, and Ark Prakash written by Maharishi Charak, Nagarjuna, and Lankapati Ravan, respectively, are the most authentic source of ancient knowledge as far as interaction of plant extracts and metal ions is concerned. Indeed, our timeworn and treasured mythology has got a new face of technology!

Nanotechnology is considered as a truly multidisciplinary field of research and development which is witnessing an exponential progress during recent times. It rises from the convergence of different disciplines of science and technology like physics, chemistry, biology, materials science, engineering science, medical science, and other sciences at nanometer (nm) scale (<100 nm), which provides ways of synthesis, characterization and manipulation of plethora of nanoparticles at nanoscale. The concept of reduction in particle size of materials is clearly provided in age-old knowledge of Ayurveda too, which utilizes the medicinal values of








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various plant and/or plant parts. So the first relation between nanoscale and human life was developed naturally in Ayurveda about 5000 year ago as an Indian system of medicine. Recently, modern science has been started exploring nanoscience and nanotechnology in twenty-first century. Ayurvedic medicine has metal nanoparticles like silver, gold, platinum, tin, zinc, iron, copper, etc. Nanoparticle has multi-functional properties based on their specific characteristics such as size, shape, distribution, and morphology. It has very broad spectrum of applications in different fields such as medicine, diagnosis, biosensors, bioimaging, targeted drug delivery, nutrition, catalysis, ultrasensitive chemical sensors, cosmetics, nanodevices fabrication, nanomedicine, agriculture, waste water treatment, cosmetics, and food industry. Apart from medical application of nanoparticles, it has been also used in electronics, magnetic, optoelectronics, energy storage, mechanics, instrumentations, and storage devices (Sondi and Salopek-Sondi 2004; Chandran et al. 2006; Song and Kim 2009; Monda et al. 2011; Bar et al. 2009; Kim et al. 2007; Joerger et al. 2000; Panigrahi et al. 2004; Oliveira et al. 2005; Sathishkumar et al. 2009; Dubey et al. 2010; Khalil et al. 2013; Ahmad et al. 2003; Popescu et al. 2010; Baruwati et al. 2009; Daniel and Astruc 2004; Dhuper et al. 2012; Kumar et al. 2014; Vivek et al. 2012; Jha and Prasad 2011a; Prasad et al. 2014, 2016, 2017). Recently, extensive work has been done on development of new drugs from natural products for the last two decades due to the reported resistance of microorganisms from the existing drugs. Nanoparticles have been synthesized through different physical and chemical processes which have their own merits and demerits. Physical and chemical methods of nanoparticle synthesis has required high energy, temperature, pressure, radiation and highly concentrated reducing and stabilizing agents that are harmful to the ecosystem. Therefore, biological synthesis/green synthesis of nanoparticles has been using less energy, low temperature and pressure and occurs in single steps that produce functionalized nanoparticles. Monodispersed and functionalized nanoparticles are challenged for biomaterials science which is synthesized by green technology with specific size, shape, and morphology. So, the green synthesis of nanoparticle has been evolving over other classical (physical and chemical) methods due to the availability of more biological entities and eco-friendly protocols which are non-toxic, non-hazardous, clean, high yield, and cost effective (Prasad 2014). Plant-mediated green synthesis of nanoparticles has been highly explored due to availability of more biodiversity, easily found in nature, and economically feasible. Indian traditional medical system has utilized approx. 600 medicinal plants for development of medicine to cure the chronic diseases during seventeenth century. These plant/plants parts contain novel phytochemicals in form of primary and secondary metabolites such as proteins, amino acids, enzymes, carbohydrates, polysaccharides, alkaloids, flavonoid, tannins, terpenoids, saponins, vitamins, and phenolic acid. A large number of medicinal plants and its various metabolites have been reported in Table 9.1. These phytochemicals (primary and secondary metabolites) have ability to reduce the metal ions into corresponding metal nanoparticles. Hence, the metabolites of different medicinal plant possess different properties and act as bioreductants, stabilizing and capping agents of synthesized nanoparticles. Medicinal plant/plant parts have been utilized to fabricate

Table 9.1 Images of plants/plants' parts with their botanical names along with their phytochemicals

Plants/parts with their botanical names and images	Phytochemicals	References
 <i>Aegle marmelos</i> (Leaf)	Akimmianine, aegelin, lupeol, cineole, citral, citronellal, cuminaldehyde, eugenol, and marmesinin	Jha and Prasad (2011a)
 <i>Mentha arvensis</i> (Leaf)	d-carvone, careen, d-sylvesterene, and citronellol	Jha and Prasad (2012)
 <i>Ocimum sanctum</i> (Leaf)	Eugenol, carvacrol, caryophyllene, limonene, and mucilage	Jha and Prasad (2012)
 <i>Eucalyptus globules</i> (Leaf)	Cineole, pinenes, sesquiterpene alcohols, aromadendrene, cuminaldehyde eugenol, and terpenoids	Jha and Prasad (2012)
 <i>Azolla sp.</i> (Leaf)	Phenolics, tannins, anthraquinone, glycosides, and sugars	Jha and Prasad (2016a)
 <i>Clerodendrum infortunatum</i> (Leaf)	Alkaloids, steroids, terpenoids, phenolics, flavonoids, tannins, and saponins	Jha and Prasad (2016b)
 <i>Eclipta alba</i> (Leaf)	Flavonoids, polyphenols, flavones, quinones, terpenoids, and organic acids	Jha et al. (2009)

(continued)

Table 9.1 (continued)

Plants/parts with their botanical names and images	Phytochemicals	References
 <i>Cycas</i> (Leaf)	Flavonoids, biflavanone, tetrahydrohinokiflavone, amentoflavone, metallothionein, phytochelatin, superoxide dismutase, catalase, glutathione, malate, citrate, oxalate, succinate, aconitate, α -ketoglutarate, peroxidase	Jha and Prasad (2010)
 <i>Azadirachta indica</i> (leaf)	Nimbin, nimbanene, nimban-diol, nimbolide, n-hexacosanol, nimbiol, azadirachtin, tartaric acid, different alkaloids, flavonoids, steroids, terpenoids, organic acids	Kumari et al. (2018a, b), Bhuyan et al. (2015)
 <i>Nyctanthes arbortristis</i> (leaf)	Carbohydrate, tannins, saponin, flavonoids, glycosides, phenols, anthraquinones, terpenoids, alkaloids, phlobotamins, and organic acids	Kumari et al. (2018a, b)
 <i>Withania somnifera</i> (Leaf)	Methyl 7-oxooctadecanoate, flavonoids, tannins, steroids, amino acids, glycosides, glucose	Nagati et al. (2012)
 <i>Acalypha indica</i> (Leaf)	Quercetin, flavonoids, phenolic compounds	Krishnaraj et al. (2010)
 <i>Aloe vera</i> (Leaf)	Biomolecules, vitamins, enzymes, lignin, saponins, salicylic acid, amino acids, and sugars	Maensiri et al. (2008)
 <i>Andrographis paniculata</i> (Leaf)	Alkaloids, flavonoids amino acids, saponins, tannins, and terpenoids	Suriyakalaa et al. (2013)
 <i>Artemisia nilagirica</i> (Leaf)	9-Octadecenoic acid (Z)-tetradecylester, Agaric acid, Tripalmitin, Ergosta-5, 7, 22-trien-3-ol, acetate, Cycloheptasiloxane, tetradecamethyl	Song and Kim (2009)






(continued)

Table 9.1 (continued)

Plants/parts with their botanical names and images	Phytochemicals	References
 <i>Tinospora cordifolia</i> (Leaf)	Alkaloids, diterpenoid lactones, glycosides, steroids, sesquiterpenoid, phenolics, aliphatic compounds, polysaccharides	Jayaseelan et al. (2011)
 <i>Melia azedarach</i> (Leaf)	Tannic acid, polyphenols, fatty acid, di-terpenoids, sterols, phenol, flavonoid, glycosides, lactones, azadirachtin, nimbin, nimboslin, quercetin, escopolnenin, azadiyeron, azadiyeradion, -14 opeksi, azadyeridon, gedonin, nimosinulnimosinolid, nimbandion, salanol, nimbinen, -6 dastilnimbinen, margozonolid, isomargozonolid, meyanetriol, salannin (its 14 derivatives), feraksinoloz, sinamat, meliasin, A and B nimbolins and limonoid	Sukirtha et al. (2012)
 <i>Cinnamomum zeylanicum</i> (Leaf)	Water-soluble organics, ascorbic acid, etc.	Sathishkumar et al. (2009)
 <i>Iresine herbstii</i> (Leaf)	Phytoalexin, isothiocyanates, allcins, anthocyanins, essentials oils, tannins, polyphenols, and terpenoids	Dipankar and Murugan (2012)
 <i>Euphorbia prostrata</i> (Leaf)	Antraquinones, protein, polyphenols, flavonoids, phenols, phlobatannins, polysaccharides, saponins, tannins, and terpenoids	Zahir and Rahuman (2012)
 <i>Mentha piperita</i> (Leaf)	Menthol, terpenoid, some essential oil	MubarakAli et al. (2011)
 <i>Piper betle</i> (Leaf)	Isoverbascoside, terpenoids, volatile oil, and tannins	Cruz et al. (2010)






(continued)

Table 9.1 (continued)

Plants/parts with their botanical names and images	Phytochemicals	References
 <i>Piper betle</i> (Leaf)	Alkaloid, tannins, chavicol, betelphenol, eugenol, allyl pyrocatechin, terpene, cineol, caryophyllene, cadinene, menthone phenyl, propane, sesquiterpene, cyneole, sugar, and some essential oil	Mallikarjuna et al. (2012)
 <i>Gelsemium sempervirens</i> (Whole)	Protein, amide, saponins, flavonoids, and carbohydrates	Das et al. (2011)
 <i>Altemanthera sessilis</i> (Whole)	Amine and carboxyl group such as proteins, amino acids, enzymes, polysaccharides, alkaloids, tannins, phenolics, saponins, terpenoids, and vitamins	Niraimathi et al. (2012)
 <i>Mirabilis jalapa</i> (Flower)	Polysaccharides, flavones, terpenoids, and proteins	Vankar and Bajpai (2010)
 <i>Rosa sp.</i> (Flower)	Monoterpene hydrocarbons, sesquiterpenes hydrocarbons, oxygenated sesquiterpenes, alkanes/alkenes, alcohols, furan derivatives (O-heterocyclic), kaempferol and quercetin, glycosides	Jha and Prasad (2013)
 <i>Citrus aurantium</i> (Fruit)	Flavonoids, vitamin C, flavanones, hesperetin, naringenin, eriodictyol, etc.	Jha et al. (2011)








(continued)

Table 9.1 (continued)

Plants/parts with their botanical names and images	Phytochemicals	References
 <i>Capsicum annuum</i> (Fruit)	<i>trans-p</i> -feruloyl- β -D-glucopyranoside, <i>trans-p</i> -sinapoyl- β -D-glucopyranoside, quercetin 3- <i>O</i> - α -l-rhamnopyranoside-7- <i>O</i> - β -D-glucopyranoside, <i>trans-p</i> -ferulyl alcohol-4- <i>O</i> -[6-(2-methyl-3-hydroxypropionyl)] glucopyranoside, luteolin 6- <i>C</i> - β -D-glucopyranoside-8- <i>C</i> - α -l-arabinopyranoside, apigenin 6- <i>C</i> - β -D-glucopyranoside-8- <i>C</i> - α -l-arabinopyranoside, luteolin 7- <i>O</i> -[2-(β -D-apiofuranosyl)- β -D-glucopyranoside], quercetin 3- <i>O</i> - α -l-rhamnopyranoside, and luteolin 7- <i>O</i> -[2-(β -D-apiofuranosyl)-4-(β -D-glucopyranosyl)-6-malonyl]- β -D-glucopyranoside	Jha and Prasad (2011b)
 <i>Caria papaya</i> (Fruit)	Hydroxyl flavones, catechins, vitamins, phenols, proteolytic enzyme	Jain et al. (2009), Jha and Prasad (2015)
 <i>Dillenia indica</i> (Fruit)	Biomolecules, lupeol, betulinaldehyde, stigmasterol, betulinic acid, beta-sitosterol, dillentin, betulin, and triterpenoids	Singh et al. (2013)
 <i>Cucumis sativus</i> (Fruit)	Glycosides, alkaloids, tannins, proteins and amino acids, phytosterols, steroids, terpenoids, saponins	Roy et al. (2015)
 <i>Allium cepa</i>	Flavonoids, alkaloids, anthocyanins, polyphenols, diallyl disulfide	Saxena et al. (2010)

(continued)

Table 9.1 (continued)

Plants/parts with their botanical names and images	Phytochemicals	References
 <i>Dioscorea bulbifera</i> (Tuber)	Diosgenin, ascorbic acid, flavonol glycosides and proteins	Ghosh et al. (2012)
 <i>Citrus sinensis</i> (Peel)	Water-soluble compounds, citric acid, ascorbic acid	Kaviya et al. (2011)
 <i>Punica granatum</i> (Peel)	Saponins, quinones, flavonoids, alkaloids, glycosides, coumarins, anthocyanin, and betacyanin	Jayaprakash and Sangeetha (2015)
 <i>Trigonella-foenum graecum</i> (Seed)	Flavonoids, proteins	Aromal and Philip (2012)
 <i>Cassia fistula</i> (Stem)	Phenol, flavonoid, proanthocyanidin, lupeol, β -sitosterol, hexacosanol	Daisy and Saipriya (2012)
 <i>Citrullus colocynthis</i> (Calli)	Polyphenols, catechin gallate, epicatechin gallate, and theaflavin	Satyavani et al. (2011)
 <i>Boswellia serrata</i> (Gum)	Protein, enzyme, α -pinene, p-cymene, d-limonene, monoterpenes, diterpenes, and sesquiterpenes	Kora et al. (2012)

different structure, shape, and size like wire, tube, and flower type of nanoparticles which works as functionalized nanoparticles. Functionalized nanoparticles have been used potentially in different areas of medical science and pharmaceutical industries such as diagnosis, therapeutics, drug delivery systems and development of advanced instruments, surgical bandages/nanodevices, and commercial products. Hence, plant-mediated nanoparticle has been considered as building blocks of the forthcoming generations to control various diseases (Jha et al. 2009; Nagati et al. 2012; Krishnaraj et al. 2010; Maensiri et al. 2008; Jha and Prasad 2016a; Sukirtha et al. 2012; MubarakAli et al. 2011; Prasad et al. 2011, 2012; Valtchev and Tosheva 2013; Weiss et al. 2006; Wang et al. 2007; Vanaja et al. 2013; Shameli et al. 2012; Gopinath et al. 2012; Amarnath et al. 2012; Prasad and Swamy 2013, Swamy and Prasad 2012; Mittal et al. 2013; Jacob et al. 2012; Kuppusamy et al. 2016; Ahmed et al. 2016; Makarov et al. 2014; Jayaprakash and Sangeetha 2015; Haverkamp and Marshall 2009; Cruz et al. 2010; Roy and Das 2015; Kumari et al. 2017; Joshi et al. 2018). This chapter will focus on synthesis of functionalized nanoparticles and its application in medical science.

9.2 Fabrication of Functionalized Nanoparticles

Nanoparticles are delineated as particulate dispersions of solid particles with at least one dimension at a size range of 10–1000 nm. When the inorganic nanoparticles are surrounded by the organic molecules as an interfacial layer to stabilize and cap them or are attached as a functional group is defined as functionalized nanoparticles. Most of the plants in nature have been possessing organically active biomolecules which are already established, and these active biomolecules (primary and secondary metabolites) act as reducing, stabilizing, and capping agents for fabrication of inorganic nanoparticles. This fabricated nanoparticle has been occurring in a single step which is non-pathogenic, economically feasible, and ecofriendly. The protocol for the fabrication of different functionalized nanoparticle involves the collection of plants/plant parts from available place, then it has to be washed thoroughly twice/thrice with tap water followed by sterile distilled water to remove associated debris. Approximately 10 gm clean and fresh source (plant/plants' part) has to be dried, cut into fine pieces, and mixed with 100 mL of 50% ethanol in a flask, and the mixture is allowed to be heated and boiled for 15 min before decanting till the color changes from clear transparent to light green (for example). The source mass is then pressed by wrapping in serene cloth and 50 mL extract (say) has to be collected under laminar flow. It has to be doubled in volume and treat it as a source extract. For the reduction of metal ions, this 50 mL of source extract is to be allowed to mix with 5 mL of 0.025 M aqueous solution of metal salt constant stirring at 60 °C on orbital-sacker. As soon as, it starts to change the color of the mixture from deep straw to different colors due to excitation of surface plasmon resonance which indicates the formation of metal nanoparticles. The synthesized nanoparticles through source extract have to be centrifuged at 5500 rpm for 15 min and subsequently re-dispersed

in de-ionized water to get rid of any uncoordinated biological molecules. Plant extracts are been used to prepare the nanoparticles, and different techniques have been employed to characterize these nanoparticles. The synthesized nanoparticles through source extract were centrifuged at 5500 rpm for 15 min and subsequently re-dispersed in de-ionized water to get rid of any uncoordinated biological molecules. Plant extracts have been used to prepare the nanoparticles, and different techniques were employed to characterize these nanoparticles. Transmission electron microscopy (TEM) and scanning electron microscope (SEM) analysis provide the size and shape of nanoparticles. The FTIR spectroscopic technique is being used to characterize the nanoparticles which define the biomolecules that have a primary amine group, carbonyl group, and hydroxyl groups, and other stabilizing functional groups bind with inorganic (metal) nanoparticles (Jha et al. 2009, 2011; Das et al. 2011; Jha and Prasad 2010, 2012; Ghosh et al. 2012; Umoren et al. 2014; Tripathy et al. 2010; Bankar et al. 2010; Ahmed and Hussain 2013; Salem et al. 2015; Premanathan et al. 2011; Azam et al. 2012; Gordon et al. 2011; Namratha and Monica 2013; Rao and Paria 2013). Figure 9.1 shows *Nyctanthes arbortristis* leaves (as an example) mediated synthesis of functionalized silver nanoparticles (AgNPs) which may be used for various biomedical applications.

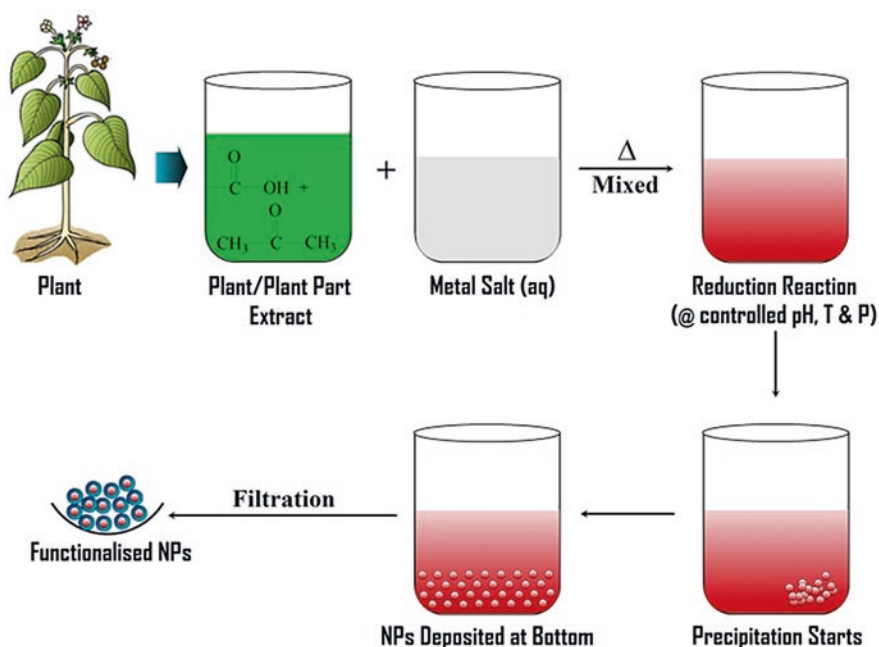


Fig. 9.1 Green synthesis of silver nanoparticles using *Nyctanthes arbortristis* leaves

9.3 Application of Functionalized Silver Nanoparticles

Functionalized nanoparticle has been attached with different types of ligands or capping agents which make chemically more flexible surfaces. This can be turned into biological tools and technique like imaging agents, fluorescent tags, biosensors, molecular scale fluorescent tags, and targeted molecular delivery vehicles which easily distinguish diseased and healthy tissue. This can provide therapy at a molecular level with the help of tools and technique, thus treating the disease and assisting in study of the pathogenesis. This has been designing the drugs with greater degree of cell specificity, more efficacy, and less adverse effects. Here, the application of functionalized silver nanoparticles (AgNPs) has been discussed in various biomedical to industrial applications such as antibacterial, antifungal, and anti-cancer (Mokhtari et al. 2009; Barkalina et al. 2014; Surendiran et al. 2009; Kumari et al. 2017; Nikalje 2015; Cormode et al. 2009; Rai et al. 2013; Han et al. 2007; Fakruddin et al. 2012; Daniel and Astruc 2004; Du et al. 2007; Fayaz et al. 2009; Fortin and Beveridge 2000; Krolukowska et al. 2003; Mallikarjuna et al. 2012; Ninganagouda et al. 2014; Valtchev and Tosheva 2013; Flores et al. 2013; Aziz et al. 2014, 2015, 2016; Ghodake et al. 2013; Liu et al. 2013; Prabhu and Poulouse 2012; Ray et al. 2011; Zhang et al. 2012; Kumari et al. 2018a, b). A schematic diagram has been representing various applications of AgNPs which is provided in Fig. 9.2.

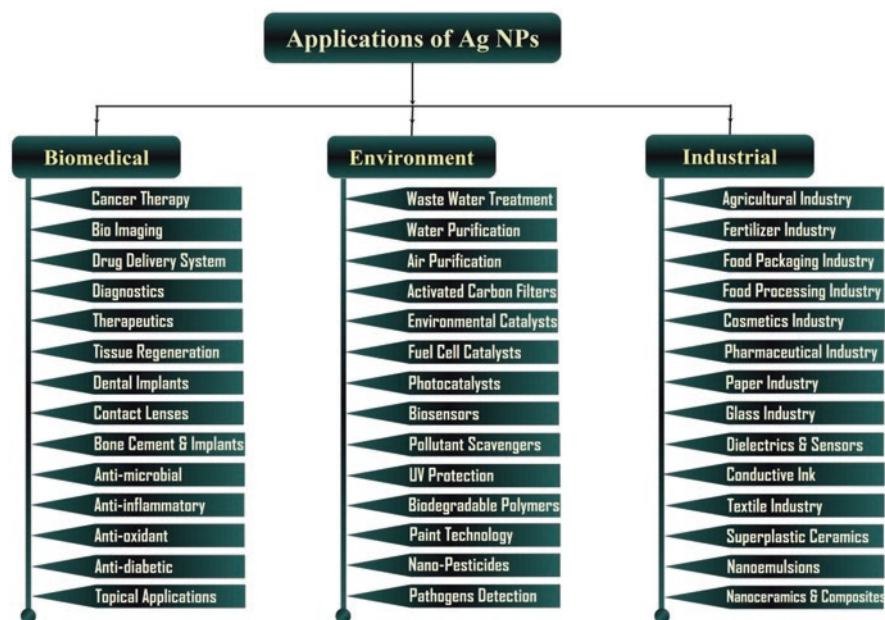
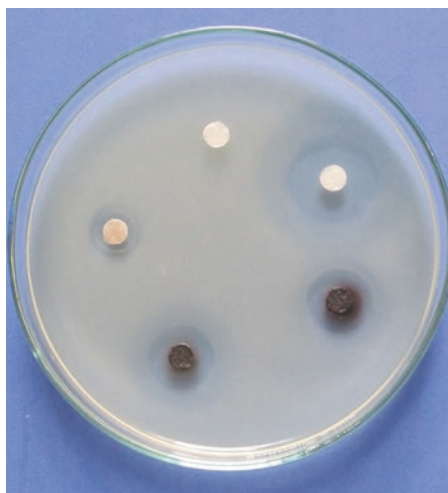


Fig. 9.2 Applications of AgNPs in different areas of science, technology, and industry

9.4 Antimicrobial Activity of AgNPs

Nanoparticle interacts with biological molecules at the nanoscale in both intracellular and extracellular manner. Nanoparticles are obtaining greater importance due to the presence of larger surface area that enables them to have a better contact with microbes as compared to their massive counterparts which shows high antimicrobial activity at the nanoscale. Hence, the various nanoparticles are being used as the potent antimicrobial agents due to the nanosize which changes the physio-chemical properties of metal and oxide. Nanoparticle is an effective and fast acting antimicrobial agent against a broad spectrum of pathogenic bacteria and fungi which have been utilized in various processes in the field of medical science. Silver nanoparticle is one of the nanoparticles which showed effective antimicrobial activity against both bacteria and fungi. The AgNPs interact with thiol group compound present in bacterial and fungal membranes which exhibit a very strong association with them to destroy the activity of bacteria (Gram-positive and Gram-negative bacteria) and fungi cells. The antibacterial activity of AgNPs was studied against *Escherichia coli* (*E. coli*) using agar well diffusion method. The zones of inhibition (clear zones) were observed after the incubation time against the test organism with dose-dependent AgNPs (Fig. 9.3). When *E. coli* cells treated with AgNPs it becomes the formation of “pits” in the bacterial cell walls showed the accumulation of AgNPs which leads to cell death. Another way to get the enhanced efficiency, the functionalized AgNPs have to be mixed with different antibiotics such as erythromycin, penicillin G, clindamycin, amoxicillin, and vancomycin and were evaluated against different microbes such as *E. coli* and *S. aureus* which showed better results. The mechanisms of the action of AgNPs in *E. coli* have been observed through the leakage of reducing sugars and proteins which induce cell death. In addition, the AgNPs not only interact with cell wall and cell membranes but it also perforates into the

Fig. 9.3 Antimicrobial activity of silver nanoparticles (AgNPs) on *E. coli*



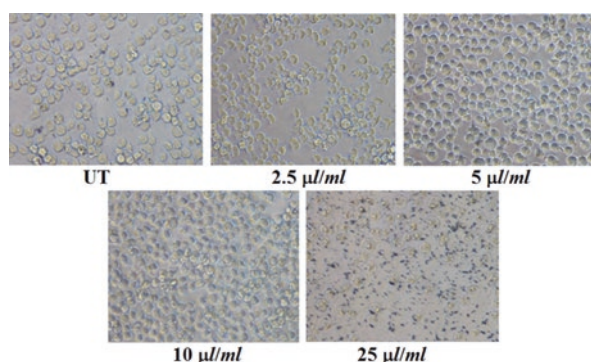
bacterial and fungal cells. After perforation of the AgNPs into the cells, it binds to the cell wall, cell membrane, genomes and inhibits the respiratory process. Therefore the presence of AgNPs inside the cell has inhibited the uptake of phosphate and the release of mannitol, succinate, proline, and glutamine molecules in *E. coli* cells. This study represents the action of AgNPs attached to the sulfur-containing proteins on the bacterial cell membrane, and it can also combine with phosphorus moieties in DNA, which inactivate the replication of DNA and enhance the membrane permeability, inhibition of enzyme functions finally leading to cell death. It shows that the active surfaces of AgNPs release the Ag-ions to induce the generation of intracellular reactive oxygen species (ROS) in bacterial cells and uncouple the electron transport system. The antimicrobial activities of these nanoparticles depend on chemisorbed Ag⁺, formed on the surface of AgNPs by dint of extreme sensitivity to oxygen. This nanoparticle have been studied to synthesize composites for use as coating materials for several mechanisms, disinfecting filters and as a medium for antibiotic delivery which have been offered to explain the inhibitory effect of AgNPs on bacteria. These have also been used to treat skin infections like burns, wounds, and healing. AgNPs appear to be alternative antibacterial agents to antibiotics and have the ability to overcome the bacterial resistance against antibiotics. Therefore, silver nanoparticles can be used as effective growth inhibitor in various microbes and they are applicable to different antibacterial and antifungal control system (Amin et al. 2012; Singhal et al. 2011; Singh et al. 2008; Sinha et al. 2009; El-Rafie et al. 2010; Geethalakshmi and Sarada 2010; Fatima et al. 2015; Verma et al. 2010; Sathishkumar et al. 2009; Durán et al. 2007; Aziz et al. 2014, 2015, 2016; Birla et al. 2009; Sharma et al. 2014; Gade et al. 2010; Bankura et al. 2012; Flores et al. 2013; Fortin and Beveridge 2000; Ghodake et al. 2013; Lokina et al. 2015; Krolukowska et al. 2003; Liu et al. 2013; Manikandan et al. 2014; Prabhu and Poulouse 2012; Ray et al. 2011; Tripathi et al. 2007; Zhang et al. 2012; Barkalina et al. 2014; Mallikarjuna et al. 2012; Surendiran et al. 2009; Nikalje 2015; Cormode et al. 2009; Ninganagouda et al. 2014; Roy et al. 2015; Rai et al. 2013; Fakruddin et al. 2012; Bindhu and Umadevi 2013; Ali et al. 2011; Amarnath et al. 2012; Zhang et al. 2016).

9.5 Anticancer Activity of AgNPs

Cancer is a disorder causing death worldwide which is characterized by an abnormal growth of cells or tissues developed through various cellular functions such as cell signaling, proliferations, and apoptosis which changes the molecular interaction within the cell. It is a second major cause of death in the human. It is treated by different methods like surgery, chemotherapy, radiotherapy, and others. These standard methods of treatments are expensive and have side effects; therefore alternatives of such treatments are urgently needed which should be inexpensive, non-toxic, and effective with minimal side effects for wider acceptability. So there are increasing demands for anticancer therapy which is a challenge to find drugs and therapies

for the treatments of various cancers. The battle against cancer is most difficult particularly in the development of therapies for multiplying several tumors. Chemotherapy has been used for the treatment of cancer but still it reveals low specificity and restricted dose to limit toxicity. Therefore the conventional methods have been developed to require the combination of controlled released technology and targeted drug delivery that is more effective and less harmful. Nanoparticles are expected to revolutionize the cancer treatment as diagnosis and therapy. It can provide unique interactions with biomolecules that may be useful in diagnosis and treatment of cancer. Recently, various nanoparticles (Ag, Au, Pt, Cu, ZnO, CuO) have been used in anticancer therapy for several types of cancer like HT-29 cell lines, Hep2 cell line, THP-1 human leukemia cell lines, Vero cell line and breast cancer lines, liver cancer cell lines (HepG2) and lung cancer cell lines (A549). In this chapter, investigation of functionalized silver nanoparticles (AgNPs) and their anticancer activity against THP-1 human leukemia cell lines has been presented. Recently, experiments observed that AgNPs induce apoptosis and sensitize cancerous cells. It can also induce alterations in cell morphology, metabolic activity, DNA damage, decreased cell viability and increased production of reactive oxygen species (ROS), which might enhance the oxidative stress leading to mitochondrial damage. The cellular uptake of AgNPs has been occurred through endocytosis. When such cells are treated with nanoparticles, they exhibit various abnormalities like upregulation of metallothionein, downregulation of major actin, myosin, and filamin binding proteins which arrest mitotic division. The morphology analysis of cancer cells observed that functionalized AgNPs could induce cell death very significantly. Figure 9.4 shows the morphological analysis of THP-1 leukemia cell line treated with different concentrations of functionalized AgNPs synthesized from *Nyctanthes arbortristis* leaf and compared with untreated cell line. The cellular and molecular mechanisms of AgNPs-treated cancerous and normal cell lines could be understood as the AgNPs are capable of adsorbing cytosolic proteins on the surface that may influence the intracellular function of the cancerous cells, which can also regulate gene expression and production of inflammatory cytokines. The AgNPs could be altering the regulation of about more than 1000 genes in a cell but among several genes, heat shock protein, metallothionein, and histone proteins are most

Fig. 9.4 Comparison of morphological changes in untreated and treated (with different concentrations of functionalized AgNPs synthesized using *Nyctanthes arbortristis* leaves) THP-1 leukemia cell line



significant. Recently, AgNPs are also inducing autophagy through the accumulation of autophagolysosomes inside cancerous cells. Autophagy is a concentration-dependent process which has a dual function, at lower level of concentration it can enhance the cell survival and at higher level of concentration it can cause cell death. Functionalized AgNPs manifested pronounced toxic effect against carcinoma cells than non-carcinoma cells which indicates that AgNPs could target cell-specific toxicity and could lower level of pH in the cancer cells. So the targeted delivery is an essential requirement for the treatment of cancer (Flores et al. 2013; Ramar et al. 2014; Banerjee and Narendhirakannan 2011; Sathishkumar et al. 2009; Lokina et al. 2015; Azzazy et al. 2012; Daisy and Saipriya 2012; Fortina et al. 2007; Fatima et al. 2015; Gan and Li 2012; Jacob et al. 2011; Jacob et al. 2012; Subramanian 2012; Safaeipour et al. 2009; Asharani et al. 2009; Sanpui et al. 2011; Guo et al. 2013; Rajeshkumar 2016; Phull et al. 2016; Majeed et al. 2018; Krishnan et al. 2016; Nagajothi et al. 2017; Majeed et al. 2016).

9.6 Conclusion

Nature has indeed been elegant and resourceful which enables us to create the most efficient miniaturized functional nanoparticles. The use of green technology for metal nanoparticles synthesis leads a desire to develop eco-friendly techniques. These functionalized nanoparticles have been used in various fields such as pharmaceuticals, diagnosis, therapeutics, sustainable energy, agriculture, environments, and other commercial products. The plant-mediated nanoparticles have projected impact on treatment and diagnosis of different diseases with controlled side effects. In future, the plant metabolites have wide perspective for the synthesis of functionalized metal nanoparticles in biomedical applications and commercial products.

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Chapter 10

Degradation Dye Using Gold and Silver Nanoparticles Synthesized by Using Green Route and Its Characteristics



S. Rajeshkumar and R. V. Santhiyaa

10.1 Introduction

Currently, Nanobiotechnology becomes very apparent in the field of research owing to its multidisciplinary role (Vanaja et al. 2013). The size of the nanomaterial extended between 1 and 100 nm (Rajeshkumar et al. 2016). Diverse procedures were carried out to synthesize nanoparticles such as physical, chemical, and biological (Menon et al. 2017). Earlier, they are used for the synthesis of nanoparticles. However, these techniques have been faced several consequences like high cost, toxicity, and production of intense heat and pressure. To overcome these issues, living organisms such as bacteria (Shahverdi et al. 2007; Rajeshkumar et al. 2013), algae (Singaravelu et al. 2007; González et al. 2013; Aziz et al. 2014, 2015), fungi (Shaligram et al. 2009; Hemath et al. 2010; Aziz et al. 2016), and plants (Salam et al. 2012; Kiruba Daniel et al. 2013; Prasad 2014) plays a key role in the eco-friendly nanoparticles. Among the other nanoparticles, gold and silver nanoparticles have numerous applications in the field of biomedical like diagnosis, therapeutic, sensors, and bio imaging (Salata 2004; Prasad et al. 2016). However, green synthesis by plants possess numerous advantages than the microorganisms owing to its easy availability, safe to handle, and also has a great potential to reduce and stabilize the nanoparticles by the presence of phytochemicals (Rajeshkumar et al. 2013; Vanaja et al. 2013, 2014; Prasad et al. 2016; Asha et al. 2017; Menon et al. 2017).

The silver nanoparticles synthesized by plants such as *Catharanthus roseus* (Ks et al. 2011), *Allium sativum* (Ahamed et al. 2011), *Parthenium* (Parashar et al.

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2009), *Mirabilis jalapa* (Vankar and Bajpai 2010), *Euphorbia hirta* (Elumalai et al. 2010), *Nicotiana tobaccum* (Prasad et al. 2011), *Syzygium cumini* (Prasad et al. 2012; Prasad and Swamy 2013), *Santalum album* (Swamy and Prasad 2012), *Vitis vinifera* (Hassan et al. 2013), *Trichodesma indicum* (Buhroo et al. 2017), *Solanum lycopersicum* (Bhattacharyya et al. 2016), and *Carissa carandas* (Joshi et al. 2018). The synthesis of gold nanoparticles using microbes such as *Penicillium denitrificans* (Bennur et al. 2016), *Bacillus stearothermophilus* (Luo et al. 2014), *Shewanella neidensis* (Suresh et al. 2011), *Staphylococcus epidermidis* (Ogi et al. 2010), *Penicillium chrysogenum* (Sawle et al. 2008), *Penicillium crustosum* (Roy and Das 2016), and *Rhizopus oryzae* (Ahmad et al. 2003; Sanghi et al. 2011). This review explains about the green synthesis of silver and gold nanoparticles and their ability in dye removal. The synthesis of different parts of plant and fruit mediated gold nanoparticles such as *Bacopa monnieri* (Babu et al. 2013), *Mangifera indica* (Philip 2010), *Mimosa pudica* (Suganya et al. 2016), *Citrus maxima* (Yu et al. 2016), *Punica granatum* (Ganeshkumar et al. 2013), *Cassia auriculata* (Venkatachalam et al. 2013), *Moringa oleifera* (Anand et al. 2015), *Cucurbita pepo* (Gonnelli et al. 2015), *Abelmoschus esculentus* (Jayaseelan et al. 2013), *Cassia fistula* (Daisy and Saipriya 2012), and *Ficus religiosa* (Wani et al. 2013) (Fig. 10.1).

10.2 Silver Nanoparticles and Silver Nanoparticles Based Nanocomposites

Table 10.1 shows the silver nanoparticles and silver nanoparticles based nanocomposites used in dye degradation (Fig. 10.2), and characters of the nanoparticles are also described. The procyanidin present in the grape seeds plays a major role in the conversion of Ag^+ into Ag NPs by forming the intermediate compound $\text{Ag}^+ - \text{procyanidin}$. Once the silver nitrate added into the seed extract solution it turns into dark brown. The direct orange dye was degraded by the process of catalytic reaction by the addition of reducing agent NaBH_4 (Ping et al. 2017). The leaf extract of *Zanthoxylum armatum* mediated AgNPs has the ability to degrade the aromatic and aliphatic compounds such as Safranin, methyl red, methyl orange, and methylene blue. From the analysis of FTIR, the biological role of *Z. armatum* can be identified as amino group and hydroxyl group indicates the presence of phenols, the nitro compound, and amine group aids to form proteins. This protein binds to the AgNPs and acts as a stabilizing agent (Jyoti and Singh 2016). Due to the scavenging activity of Ag, it trapped the electrons acquired on the Cu_2O catalyst and Ag^+ ions turned into metallic Ag once it gets reacted with the electrons. The Cu_2O system helps to degrade the methyl orange dye (Jiana et al. 2016). The exopolysaccharide surface is capable of degrading the azo dyes. The AgNPs weakens the azo-double bond by binding to the nitrogen bond, sulfur, and oxygen atoms of the azo dye through conjugation process. The hetero atoms present in the EPS exhibit the hydrophilic interaction between the azo dyes; this may bring the dye in close contact with the

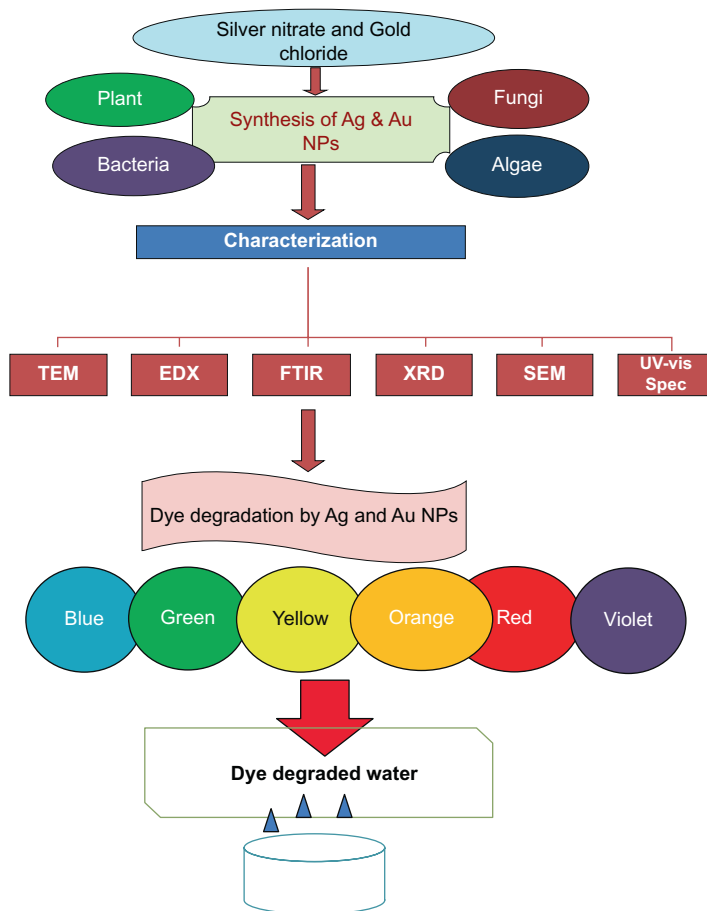


Fig. 10.1 Green synthesis of silver and gold nanoparticles in dye degradation

catalytic sites (Saravanan et al. 2017). The egg shell of *Anas platyrhynchos* mediated AgNPs plays a vital role in the degradation of harmful dyes. The FTIR analysis was done to find out the functional groups and biomolecules present in the egg shell that are responsible for reducing and stabilizing the nanoparticles. The presence of functional groups such as O-H, C=C, C=O, and N-H interprets the presence of collagen in the egg shell. It consists of glycine, aminoacids, hydroxyproline, and hydroxylysine components which help to stabilize the nanoparticles (Sinha and Ahmaruzzaman 2015a). *Achillea millefolium* and peach kernel shell are used for the synthesis of AgNPs due to its biological activities. The phenolic compounds include flavonoids and phenol carbonic acids are present in the *Achillea millefolium L.* which has the ability to reduce metallic ions and synthesizing nanoparticles. It also plays an efficient role in the degradation of hazardous dye by the process of catalytic reaction due to its low-commercial value (Khodadadi et al. 2017a). The silica

Table 10.1 Silver nanoparticles and its based nanocomposites characteristics and its dye removal

S. no.	Nanoparticles or nanocomposites	Reducing or stabilizing agent	Characteristics	Applications	References
1	Silver nanoparticles	Grape seed extract	TEM, EDX SIZE = 54.8 nm	Direct Orange dye 26	Ping et al. (2017)
2	Silver nanoparticles	<i>Zanthoxylum armatum</i>	SEM, TEM, SAED, EDS, XRD SIZE = 15–50 nm	Methylene blue, Methyl red, Safranin, and Methyl orange	Jyoti and Singh (2016)
3	Silver doped Cu ₂ O catalyst	–	–	Methyl orange	Jiana et al. (2016)
4	Silver nanoparticle	Exopolysaccharide	TEM, SEM, AFM SIZE = 35 nm SHAPE = spherical	Congo red and Methyl orange	Saravanan et al. (2017)
5	Silver and gold-silver core shell NPs	Anas platyrhynchos (egg shell)	TEM, STEM, XRD, SAED For Ag, SIZE = 6–26 nm SHAPE = spherical For Au-Ag NPs, TEM, STEM, XRD, SAED = 9–18 nm SHAPE = spherical and oval	Methylene blue, Methyl violet 6B, and Rose Bengal	Sinha and Ahmaruzzaman (2015a)
6	Silver nanoparticles	<i>Achillea millefolium</i> L. and peach kernel shell	–	Methylene blue, 4-Nitrophenol and Methyl orange	Khodadadi et al. (2017a)
7	Silicon dioxide NPs, silver and gold coated with SiO ₂ NPs (core shell)	Nanocore and Nanoshell	TEM SIZE = SiO ₂ = 30–10 nm, Ag NPs = 20–5 nm, and Au NPs = 15–3 nm	Methyl orange	Badr and Mahmoud (2007)
8	Silver nanoparticle	<i>Gmelina arborea</i> (fruit extract)	TEM, HRTEM, SAED SIZE = 8–32 nm SHAPE = spherical and crystalline	Methylene blue	Saha et al. (2017)
9	Silver and gold nanoparticles	<i>Punica granatum</i> (pomegranate juice)	TEM SIZE = for AgNPs = 36 nm, for AuNPs = 18 nm SHAPE = spherical	Cationic phenothiazine dye, anionic mono azo dye, and cationic fluorescent dye	Meenakumari and Philip (2015)

S. no.	Nanoparticles or nanocomposites	Reducing or stabilizing agent	Characteristics	Applications	References
10	Silver nanoparticle	<i>Terminalia cuneata</i> (bark extract)	XRD, DLS, HRTEM, EDS SIZE = 2.5–50 nm SHAPE = spherical	Direct Yellow 12 dye	Edison et al. (2016b)
11	Silver nanoparticle	<i>Polygonum hydropiper</i> (plant)	FTIR, FESEM SIZE = 60 nm SHAPE = spherical and aggregated into irregular structure	Methylene blue	Bonnia et al. (2016)
12	Silver nanoparticle-titanium dioxide (nanocomposite)	<i>Carpobrotus acinaciformis</i> (leaf and flower extract)	FTIR, FESEM, XRD, EDS SIZE = 20–50 nm	Congo red and Methyl orange	Rostami-Vartooni et al. (2016)
13	Silver nanoparticles	<i>Biophytum sensitivum</i> (leaf extract)	FTIR, XRD, and HR-TEM SIZE = 19.06 nm SHAPE = spherical	Methylene blue and Methyl orange	Joseph and Mathew (2015a)
14	Silver nanoparticles	(Palm shell extract)	UV, IR, XRD, TEM, EDX and Raman analysis SIZE = 50 nm SHAPE = clusters	Reactive blue-21 dye, Copper phthalocyanine-based dye, Reactive blue-21, Rhodamine-6G, and Xanthene dye	Vanaamudan et al. (2016)
15	Silver nanoparticles	<i>Mussaenda erythrophylla</i> (leaf extract)	SEM, XRD, EDAX, FTIR, PCS SIZE = 0.1–10,000 SHAPE = crystallite	Methyl orange dye and toxic azo dyes	Varadavenkatesan et al. (2016)
16	Silver nanoparticles	Cationic cetyl trimethyl ammonium bromide (surfactant)	TEM, FTIR, SEAD SIZE = 5–20 nm SHAPE = spherical, truncated triangular highly Poly-dispersed	Methyl orange	Zaheer and Aazam (2017)
17	Silver nanoparticles	Montmorillonite (clay)	XRD, FTIR, SEM, BET, EDX SIZE = 12 + -2 nm	Methylene blue	Wang et al. (2017)

(continued)

Table 10.1 (continued)

S. no.	Nanoparticles or nanocomposites	Reducing or stabilizing agent	Characteristics	Applications	References
18	Graphene oxide-silver nanoparticles (GO-AgNPs)	<i>Picrasma quassoides</i> (bark extract)	SEM-EDX, TEM-SAED SIZE = for AgNPs = 17.5–66.5 nm For GO-AgNPs = 10–49.5 nm SHAPE = spherical and crystallite	Methylene blue	Sreekanth et al. (2016)
19	Silver nanoparticles	Aqueous extract of tea	FTIR, XRD, TEM SIZE = 45 nm SHAPE = tonispherical	Ethyl violet and Methylene blue	Qing et al. (2017)
20	Silver nanoparticles	<i>Sterculia acuminata</i> (fruit extract)	XRD, TEM, FTIR, PSA SIZE = 10.3 nm SHAPE = crystallite and spherical	Methyl orange, Direct blue 24, Methylene blue, 4-Nitrophenol and Phenol red	Bogireddy et al. (2016)
21	Silver nanoparticles	<i>Lagerstroemia speciosa</i>	FTIR, XRD, TEM SIZE = 12 nm SHAPE = spherical	Methyl orange and methylene blue	Sai Saraswathi et al. (2017)
22	Silver nanoparticles	<i>Dimocarpus longan</i>	XRD, TEM, FTIR SIZE = 40 nm SHAPE = face-centered cubic structures	Methylene blue, 4-Nitrophenol, and 4-Aminophenol	Khan et al. (2016a)
23	Silver nanoparticles (AgNPs)	<i>Cicer arietinum</i> (chick pea)	DLS, TEM, EDAX, and FTIR SIZE = 88.8 nm SHAPE = spherical	4-Nitrophenol, Methylene blue and Congo red	Arya et al. (2017)
24	Silver nanoparticles (AgNPs)	<i>Ulva lactuca</i> (seaweed)	FTIR, HRSEM, XRD SIZE = 48.59 nm SHAPE = spherical	Methyl orange	Kumar et al. (2013)

25	Silver nanoparticles AgNPs	<i>Trigonella foenum-graecum</i> seeds	TEM, HRTEM, SAED, FTIR, XRD SIZE = 22 nm, 28 nm, and 32 nm SHAPE = polycrystalline	Methylene blue, Methyl orange, and eosin	Vidhu and Philip (2014)
26	Au and AgNPs	<i>Costus pictus</i> (leaf extract)	FTIR, SEM, DLS, EDX SIZE = for CPAgNPs = 46.7 nm CPAuNPs = 37.2 nm SHAPE = spherical	Methylene blue and Methyl red	Nakkala et al. (2015)
27	AgNPs	<i>Mesoporous titania</i>	XRD, EDX, HRTEM, DRS, FESEM SIZE = 34 and 18 nm SHAPE = crystallite	Methylene blue and indigo carmine dyes	Abdel Messih et al. (2017)
28	AgNPs	<i>Anacardium Occidentale Testa</i>	FTIR, XRD, HRTEM, EDS SIZE = 25 nm SHAPE = distorted spherical	Congo red and Methyl orange	Edison et al. (2016a)
29	AgNPs	Aqueous medium using starch	FTIR, XRD and HR-TEM SIZE = 18.2 ± 0.97 nm SHAPE = spherical	Methyl orange and Rhodamine	Joseph and Mathew (2015b)
30	AgNPs	<i>Cirsium japonicum</i>	HRTEM, XRD, FTIR, EDX SIZE = 2-8 nm SHAPE = spherical and no aggregation	Bromo phenyl blue	Khan et al. (2016b)

(continued)

Table 10.1 (continued)

S. no.	Nanoparticles or nanocomposites	Reducing or stabilizing agent	Characteristics	Applications	References
31	Silver-graphene oxide (Ag/GO) Nanocomposite	–	TEM, HRTEM, FTIR XRD SIZE = 9.22 ± 0.18 nm SHAPE = crystallite	Congo red and Bismarck brown	Borthakur et al. (2017)
32	Silver nanoparticles (AgNPs)	Ag/clonipitolite— <i>Vaccinium macrocarpon</i> (fruit extract)	TEM, FTIR, EDS SIZE = 15–30 nm SHAPE = spherical	Methyl orange, Methylene blue, Rhodamine B, and Congo red	Khodadadi et al. (2017b)
33	Silver phosphate/graphene nanocomposite (Ag ₃ PO ₄ /G)	–	–	Heterocyclic dye, indigo dye, anthraquinone dye, and azo dye	Xu et al. (2017)
34	Silver nanoparticles AgNPs	<i>Caralluma edulis</i>	HRTEM, FTIR, XRD, EDX SIZE = 2–10 nm SHAPE = spherical and crystallite	Bromothymol blue	Khan et al. (2016c)
35	Silver capped on commercial diamond NPs	–	–	Methylene blue, Orange II, Acid Red 1 and Rhodamine B	Manickam-Periyaraman et al. (2016)
36	Silver nanoparticles AgNPs	<i>Polygonum hydropiper</i>	FESEM SIZE = 60 nm SHAPE = spherical and aggregated in irregular form	Methylene blue	Bonnia et al. (2016)
37	Silver nanoparticles AgNPs	<i>Mussaenda erythrophylla</i> (leaf extract)	SEM, XRD, EDAX, FTIR, PCS SIZE = 0.1–10,000 nm SHAPE = crystallite	Methyl orange	Varadavenkatesan et al. (2016)
38	Silver nanoparticle and colemanite ore waste Nanocomposites	–	TEM, XRD, XPS, BET SIZE = 5–30 nm SHAPE = spherical	Reactive Yellow 86 and Reactive Red 2	Yola et al. (2013)

39	Silver nanoparticle (AgNPs)	<i>Thymbra spicata</i> (leaf extract)	FESEM, TEM, XRD, EDS, FTIR SIZE = 7 nm SHAPE = crystallite	4-Nitrophenol, Rhodamine B, and Methylene blue	Veisi et al. (2018)
40	Silver nanoparticle- <i>Solanum nigrum</i> (Sn-AgNPs)	-	FTIR, TEM, XRD SIZE = 20 and 30 nm SHAPE = spherical	Degradation of dye effluent	Malaikozhundan et al. (2017)
41	Silver nanoparticle (AgNPs)	<i>Morinda tinctoria</i> (leaf extract)	XRD, SEM, EDX, FTIR SIZE = 79–96 nm SHAPE = spherical and rod	Methylene blue	Vanaja et al. (2014)
42	Silver nanoparticle (AgNPs)	<i>Tangerine peel</i> (orange peel)	SIZE = 30.29 ± 5.1 nm, 16.68 ± 5.7 nm, and 25.85 ± 8.4 nm SHAPE = spherical	Methyl orange	Alzahrani (2015)
43	Silver nanoparticles (AgNPs)	<i>Lagerstroemia Speciosa</i>	XRD, HRTEM SIZE = 12 nm SHAPE = spherical	Methyl orange	Saraswathi and Santhakumar (2017)
44	Silver nanoparticles (AgNPs)	<i>Gracilaria corticata</i> (red algae)	HRSEM SIZE = <100 nm SHAPE = spherical	Malachite green	Poornima and Valivittan (2017)
45	Silver nanoparticles (AgNPs)	<i>Hypnea musciformis</i>	SEM, XRD, AFM, FTIR SIZE = for 2D view = 2–55.8 nm. SHAPE = spherical SIZE = for 3D view = 12 nm SHAPE = crystalline	Methyl orange	Ganapathy Selvam and Sivakumar (2015)
46	Silver nanoparticle (AgNPs)	<i>Amaranthus gangeticus</i> Linn (leaf extract)	HR-TEM, SAED, FTIR SIZE = 11–15 nm SHAPE = globular	Congo red	Kolya et al. (2015)



Fig. 10.2 Role of silver nanoparticles in dye degradation

(core shell) coated AgNPs and AuNPs core showed an excellent activity in reduction of methyl orange dye by photocatalytic degradation under xenon lamp (Badr and Mahmoud 2007). The availability of biomolecules (polyphenols, caffeine, proteins, polysaccharides, aminoacids) and phytochemicals in the fruit extract of *Gmelina arborea* plant has the properties of reducing the metal ions and stabilizing the nanoparticles by the eco-friendly green synthesis method (Saha et al. 2017). By doing the FTIR analysis, the biomolecules that are attached to the surface of the metallic ion can be identified. The presence of biomolecules such as phenolic hydroxyl, peptide bond, and carboxyl group in the *Punica granatum* acts as both stabilizing and reducing agent. The phenolic hydroxyl compound is involved during the reduction process of the metallic ion. The Ag mediated *Punica granatum* nanoparticles are very potential to degrade the anionic mono azo dye cationic phenothiazine and fluorescent types of dyes (Meenakumari and Philip 2015). The bark extract of *Terminalia cuneata* are rich in various phytochemical constituents such as polyphenols, tannic acids, gallic acid, flavanoids, phytosterol, ellagic acid, and triterpenoid saponins with high numbers. These phytoconstituents act as a reducing agent for the conversion of silver ions to silver atoms and for stabilizing the nanoparticles. These biological activities in *Terminalia cuneata* were analyzed by the

performing FTIR analysis (Edison et al. 2016b). The FTIR analysis indicates the presence of phenolic compound, hydroxyl group, free amines, carbonyl, and proteins in the plant of *Polygonum hydropiper*. These biomolecules help in the formation AgNPs by reducing the ions and stabilizing the NPs with appropriate capping agent (Bonnia et al. 2016). The extract of *Carpobrotus acinaciformis* is used as a stabilizing and reducing agent for production the immobilized AgNPs on the surface of titanium due to its phenolic and flavanoids constituents (Rostami-Vartooni et al. 2016). The FTIR analysis determined the presence of phenolic and flavonoid in the leaf extract of *Biophytum sensitivum* which plays a major role in both stabilizing and reducing agent (Joseph and Mathew 2015a). The polyphenols present in the palm tree extract were used as a capping agent for the synthesis of silver nanoparticles. The FTIR reveals that the presence of phenols, polysaccharides, and proteins in the palm shell extract act as a reducing and stabilizing agent. The silver nanoparticles have shown extraordinary performance in degrading the cationic and anionic dye using catalytic reaction (Vanaamudan et al. 2016).

10.3 Gold Nanoparticles and Gold Nanoparticles Based Nanocomposites

Table 10.2 shows gold nanoparticles and gold nanoparticles based nanocomposites, characteristics and dye degradation were elucidates (Fig. 10.3). The nanocomposites of gold-sodium niobate were synthesized by the hydrothermal method. The Au doped NaNbO₃ nanocomposite using dye degradation was carried out by photocatalytic degradation under visible light. While comparing to gold nanoparticle, the gold doped nanocomposites shows a greater performance in degrading the malachite green dye (Baeissa 2016). The leaves extract of *Dalbergia coromandeliana* expressed an excellent activity towards the dye degradation due to the presence of phytoconstituents such as terpenoids, neoflavonoids, steroids, and isoflavonoids. These play a vital role in reducing the Au ions into Au atoms by donating the electron and hydrogen atom as well as stabilizing the nanoparticles with the binding agent (Umamaheswari et al. 2018). From the study of FTIR, it was identified that the presence of these functional groups (O-H, C=O, and N-H) denotes the availability of the protein in the egg shell extract. These functional groups get involved in the production of NPs and act as both reducing agent and capping agent. The dye degradation was carried out by catalytic reaction (Sinha and Ahmaruzzaman 2015b). Carboxylic acids, nitro compounds, aromatic and aliphatic amines, and alkanes are the functional groups present in the flower extract of *Plumeria alba*. From the FTIR analysis, it has been detected that the presence of these functional groups makes the efficient binding between the *Plumeria alba* and gold nanoparticles for the production and capping of PAGNPs. Due to the catalytic reaction, the 4-nitrophenol reduced into 4-aminophenol (Mata et al. 2016). For the first time, the gold nanoparticles were developed extracellularly from the cell-free extract of *Bacillus*

Table 10.2 Characterization of gold nanoparticles and its dye removal

S. no	Nanoparticles or nanocomposites	Reducing or stabilizing agent	Characteristics	Applications	References
1	AgNPs, Au-AgNPs core shell NPs	Anas platyrhynchos (egg shell)	FTIR, TEM, SAED, STEM, XRD, EDAX = for AgNPs, 6–26 nm. SHAPE = spherical For Ag-AuNPs = 9–18 nm. SHAPE = spherical and oval	Rose Bengal, Methyl Violet 6B, and Methylene blue	Sinha and Ahmaruzzaman (2015a)
2	Au/NaNbO ₃ Nanocomposite	–	TEM, XRD SIZE = 50 nm SHAPE = nanocube structure	Malachite green	Baeissa (2016)
3	Gold nanoparticles (AuNPs)	<i>Dalbergia coromandeliana</i>	HRTEM, XRD, SAED, FTIR = 532 nm SHAPE = crystalline	Congo red and methyl orange	Umamaheswari et al. (2018)
4	AuNPs	Egg shells of Anas platyrhynchos	TEM, SAED, FTIR = 540–880 nm	Eosin Y dye	Sinha and Ahmaruzzaman (2015b)
5	AuNPs	<i>Plumeria alba</i> (flower extract)	TEM, EDAX, XRD, FTIR = 28 ± 5.6 and 15.6 ± 3.4 nm SHAPE = spherical	Methylene blue, eosin Y, 4-nitrophenol, methyl red, Congo red, and ethidium bromide	Mata et al. (2016)
6	AuNPs	<i>Bacillus marisflavi</i>	XRD, FESEM, TEM and DLS = 14 nm SHAPE = spherical, face-centered cubic structures	Congo red into a naphthylamine and phthalic acid and methylene blue to 2-methyl benzothiazole	Nadaf and Kanase (2016)
7	AuNPs	Sodium rhodizonate	TEM, SEM, XRD = 11 nm–7 nm	4-Nitrophenol, Methyl orange and Methylene blue	Islam et al. (2017)
8	AuNPs	<i>Aspergillus</i> sp.	TEM = 12–48 nm SHAPE = spherical and pseudo-spherical	2-Nitrophenol, 3-nitrophenol, 4-nitrophenol, o-nitroaniline and m-nitroaniline	Qu et al. (2017)

(continued)

Table 10.2 (continued)

S. no	Nanoparticles or nanocomposites	Reducing or stabilizing agent	Characteristics	Applications	References
9	AuNPs	<i>Suaeda Fruticosa</i> (plant extract)	XRD, HRTEM, SEM, and FTIR SIZE = 6–8 nm SHAPE = spheroid	Phenolic azo dyes	Khan et al. (2017)
10	Au/polydimethyl-L aminoethyl acrylate brushes (PDMAEMA)/RGO Nano hybrids	–	FTIR, XRD, TEM = 200 to 800 nm SHAPE = spherical and worm	Rhodamine B, Methyl orange and Eosine Y	Mogha et al. (2017)
11	AuNPs	<i>Sterculia acuminata</i> (fruit extract)	XRD, TEM, FTIR = 9.37–38.12 nm SHAPE = spherical	4-nitrophenol, Methylene blue, methyl orange, and direct blue 24	Bogireddy et al. (2015)
12	AuNPs	<i>Pogostemon benghalensis</i> (leaf extract)	XRD, TEM, FTIR = 10–50 nm SHAPE = spherical and triangular	Methylene blue	Paul et al. (2015)
13	AuNPs	<i>Mimosa pudica</i>	XRD, TEM, HRTEM, FTIR = 16 nm SHAPE = spherical with narrow	Rhodamine B and o-nitrophenol	Devi et al. (2015)
14	Gold nanoparticles-titanium dioxide (Au/TiO ₂)	<i>Cinnamomum tamala</i> (leaf extract)	FTIR, TEM, XRD SIZE = 8–20 nm SHAPE = crystalline	Methyl orange	Naik et al. (2013)
15	AuNPs	Kashayam, Guggulutiktham	TEM, XRD, FTIR SIZE = 15–50 nm SHAPE = crystallite	Methylene blue	Suvith and Philip (2014)

marisflavi isolated from the estuaries. It has been proved that this organism has the ability to degrade the organic dyes such as methylene blue into 2-methyl benzothiazole and congo red into alpha naphthylamine. From the FTIR studies, the functional groups which are responsible for the reduction and capping process were identified such as amine, aldehyde, and the functional groups of protein. The cell-free extract mediated gold nanoparticles were bound to the proteins and the aldehydes via conjugation process (Nadaf and Kanase 2016). The gold nanoparticles carried on the cellulose fibers have high catalytic activity. These catalysts that have been employed in the catalytic reaction of organic dyes include methyl orange, 4-nitrophenol, and methylene blue. Sodium rhodizonate acts as both reducing and stabilizing agent (Islam et al. 2017).

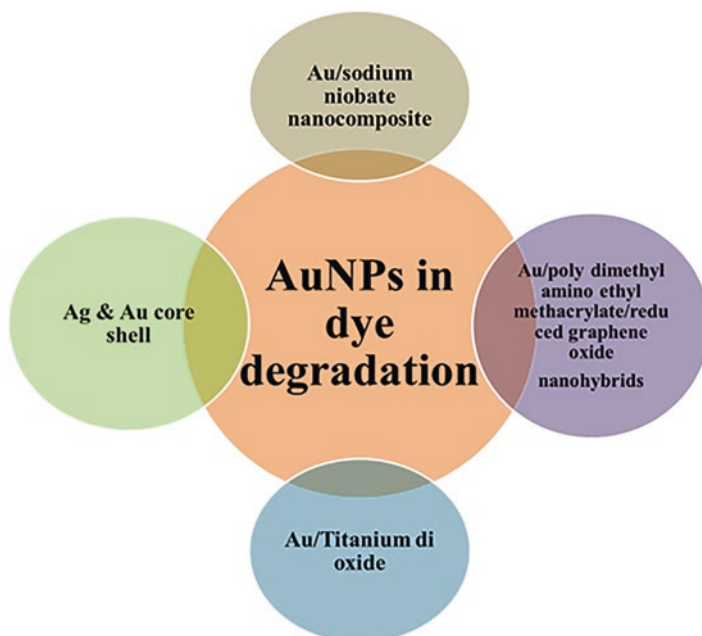


Fig. 10.3 Role of gold nanoparticles in dye degradation

10.4 Conclusion

Previously, several studies have been proved that the silver and gold nanoparticles possess various beneficial activities. Hence, this review proves that the green synthesis of silver and gold nanoparticles plays a prominent role in the degradation of hazardous dyes such as direct orange 26, methylene blue, congo red, rose Bengal, Safranin, 4-nitrophenol, 4-aminophenol, methyl red, methyl orange, rhodamine B, indigo, cationic phenothiazine dye, eosin, acid red, reactive red 2, direct yellow, m-nitroaniline, o-nitroaniline, bromophenyl blue, malachite green, rhodamine-6G, ethidium bromide, 2-nitrophenol, 3-nitrophenol, Bismarck brown, reactive yellow 86, xanthene dye, anionic mono azo dye, and ethyl violet.

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Chapter 11

Nanomaterials: An Upcoming Fortune to Waste Recycling



Mugdha Rao, Anal K. Jha, and Kamal Prasad

11.1 Introduction

The role of nanotechnology in waste minimization is an oozing trend as it deals with the dual concept of “from waste to treat waste” and “from waste to valuable products.” Nanotechnology is definitely a province that encircles subject matters like biology, materials science, and chemistry. It handles maneuvering materials at nanoscale called nanoparticles (NPs). Nanomaterials are cobbled up through either of the two approaches: (a) bottom up and (b) top down. Bottom-up way is the preferred one as the nanofabrication occurs through atom by atom, molecules by molecules stacked to obtain thermodynamically controlled composition of nanomaterial. Gibbs free energy found to be whimsical in such stacking process (Rao et al. 2017a). Nanostructures developed through biological process follows bottom-up approach. Top-down approach requires a progenitor material that undergoes reduction either through chemical or physical method (Gade et al. 2010). Waste mediated NPs (WMNPs) are fabricated mostly through biological (Bankar et al. 2010; Kaviya et al. 2011; Ahmad et al. 2012; Edison and Sethuraman 2013; Shankar et al. 2014) and chemical route. Chemical methods for synthesizing WMNPs involves irradiation-assisted chemical method (Park et al. 2014), pyrolysis (Rajarao et al. 2014; Wu et al. 2016; Kumar et al. 2014), and CVD (chemical vapor deposition) (Hintsho et al. 2014; Hintsho et al. 2016; Suriani et al. 2016; Wu et al. 2017).

The caption “waste” is not at all neoteric to us rather it has spawned facilely than anything else could have. An unforeseen jack up in residents and their comforts in accretion to their hustled lifestyle has crowned waste at the top. Nowadays,

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researchers are dynamically involved to combat waste to prevent ecological pollution in turn lives on the globe. Merely working on pollution control at the level of academics is not solely to be advantageous rather public awareness is of prime importance. Nanotechnology in the context of environmental remediation is blooming rapidly (Fig. 11.1). The reason could be the effective pertinence of nanomaterial that helps in simplifying the treatment steps, which in turn effects the time, cost, and energy requirement for executed process (Dermatas et al. 2018).

The chapter details about the waste classification in brief and then followed up by general waste management concept. Further role of nanotechnology at omnifarious scaffolds of waste management like prevention, reduction, reuse, recycle, energy recovery, and disposal were elaborated. The chapter aimed at conveying that nanotechnology might be an option other than conventional one to waste utilization. Nanomaterial fabrications from variegated sources like garbage, combustible materials, ash, pharmaceuticals, agricultural and microbial waste are accompanied in this chapter. The application of WMNPs is also brought into the limelight. In the immediate future, nanotechnology will roll on through the speculation of scale up in utilization of waste to prevent biosphere pollution.

11.2 Classification of Wastes

Before getting into details about types of waste, a question to be answered, “What is the purpose of classifying waste? Is it really important?” Definitely a big Yes! According to Lymer (2016), the storage, treatment, and its disposal are very dependent on the category to which waste belongs. Further, it aids in deciding the error-free landfill sites.

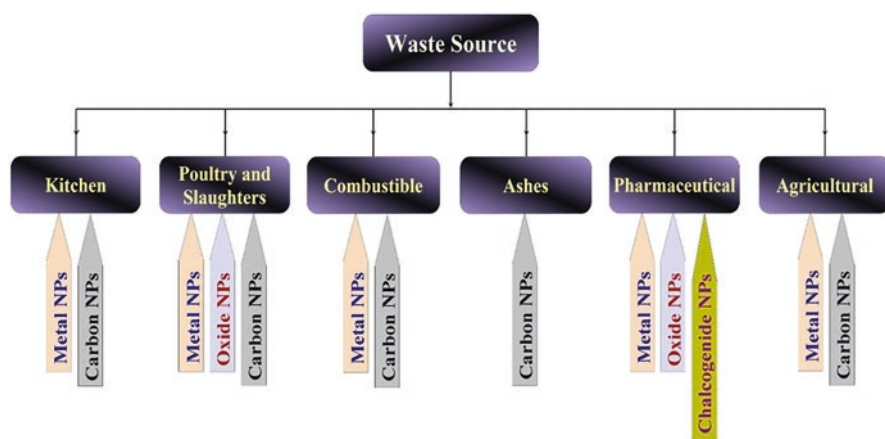


Fig. 11.1 Flow diagram of different groups of NPs fabricated from various waste source as an indication of nanotechnology role in environmental remediation

The expression “waste” hails from the Latin sound vastus that expresses unoccupied or uncultivated. Although waste can be ascertained in multiple ways but in agreement to Basel Convention of the Control of Transboundary Movements of Hazardous Wastes and their Disposal, 1989 “wastes” are the substances, which are spaced out or are intended to be spaced out of or required to be spaced out by provisions of rational law. Although classifying refuse is a tedious task, there is no unique concept of categorizing all types of waste. In depth, it is indeed the role of chemist to categorize waste as hazardous or non-hazardous.

As per our intellection, systematizing waste depends on the context in which we are working into like various fountainhead of waste in the locality, industrial scale, or the fractional elements of the offal. In coalition with execution of nanotechnology in waste conversion to valuable products, classification of waste is mentioned in Table 11.1. We have classified waste into six categories as per their origination source and the burden they create. Primary source of approximately all the offal are either households or the industries.

11.3 Waste Management (General Concept)

The escalating population with time is also raising the quantity of waste globally. There are numerous waste source concisely named to be industrial and municipal solid waste. But the uppermost concern is waste management. Not only the management methods are required to be updated rather folk educational awareness towards minimization of waste generation and its management, that too at personal level must be polished. We have seen common folks in developing countries like ours receiving immense pleasure after burning the waste as such in the context of cleaning up the area overcrowded with garbage. Waste management in developed homeland is quite contrastive to developed countries. Having clean and hygienic environment is the most favorable one because we are alive due to air that we breathe, the water that we drink, and the surroundings where we live. Waste

Table 11.1 Classification of waste as per their source of origin

Classification	Origin point	Burden
1. Garbage	Domiciliary/merchandise	Kitchen waste (food), poultry/slaughter house
2. Settlings	Domiciliary/retailer	Dead leaves, wood wool, shredders waste, waste tyre rubber, polyethelene, plastic bottles, etc.
3. Ashes	Households/industries	Rice husk ashes, coal fly ashes
4. Pharmaceuticals	Industries/households	Expired medicines, scraps etc.
5. Waste microbes	Industries/laboratories	Metal ion-treated cells, fungi refusals, bacterial cellulose discard, etc.
6. Agricultural waste	Beverage industries/food processing industries	Palm oil mill effluent, defatted seeds, orange peels, etc.

management is the sequential interconnected system that comprises of 6 gears and is depicted in Fig. 11.2.

In correspondence to the waste hierarchy, deterrence of waste generation is of utmost importance. If the waste prevention step is surpassed, then the hierarchical steps will be followed. Apart from the above steps to be followed, after disposal monitoring of the area is also a concern. According to Demirbas (2011), pyrolysis-incineration, landfill, and biogas production are the reassuring waste treatment processes. In another Handbook (2014), he has mentioned treatment methods for municipal waste like sanitary landfill, incineration, gasification, biodegradable process, composting, and anaerobic digestion. These followed-up treatment protocol that has its own gratification and hindrance is depicted in Table 11.2.

Although there are enormous methods of waste disposal, many more has to be seized into account as nanotechnology-based waste conversion to unburden the load on conventional protocols. Above all if we concentrate much on reduction of waste generation that will actually benefit in controlling environmental pollution. It is well exemplified by Rahman (2000) in his guide that reducing dependency on plastic bags, plastic film containers, tin can, rubber boot sole, plastic cups, aluminum can, cigarette butt, disposable diaper, plastic bottle, glass bottle, etc. will save the environment to a great extent.

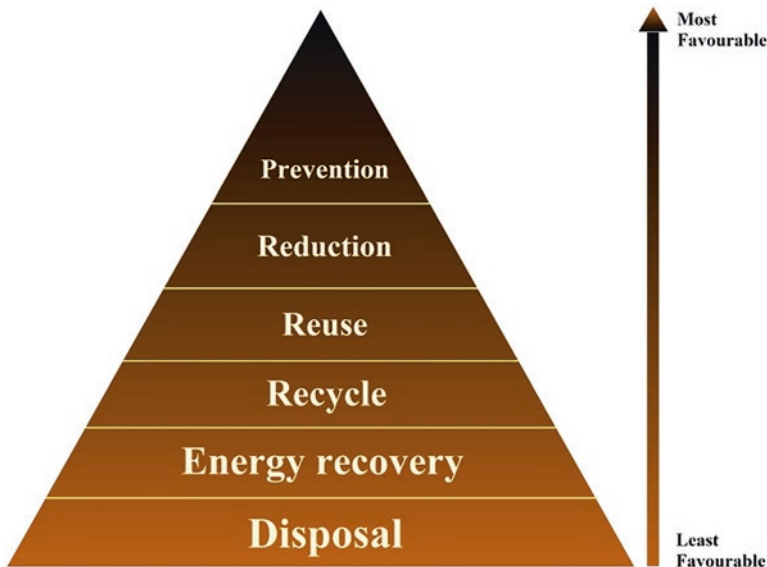


Fig. 11.2 Waste management steps detailed as pyramid format in context of favorability

Table 11.2 Waste treatment method protocols pros and cons

Process	Advantages	Disadvantages
Sanitary landfill	<ul style="list-style-type: none"> – No emission of methane and toxic gases – Limited land/water table contamination – No bad odor – No problem created by birds/rodents 	<ul style="list-style-type: none"> – Designing cost – Land requirement
Incineration	<ul style="list-style-type: none"> – Size of waste reduce – Reduction in dumping – No disease causing issues 	<ul style="list-style-type: none"> – Air pollution – Toxic gases emission – Ash treatment requirement – High maintenance cost
Gastrification	<ul style="list-style-type: none"> – Gas handling is easier – No hazardous gas emission – Less ash production 	<ul style="list-style-type: none"> – Costly maintenance – Tar and volatile poison release
<i>Biodegradation process</i>		
(a) Composting	<ul style="list-style-type: none"> – Recycling of waste – Generate manure – Cost-effective 	<ul style="list-style-type: none"> – Time consuming – Odor problem – Attract birds and rodents
(b) Anaerobic digestion	<ul style="list-style-type: none"> – Less energy requirement – Simple construction 	<ul style="list-style-type: none"> – Pre-processing of slurry – Sludge disposal – Odor problem – Maintenance of plants
(c) Waste stabilization pond system	<ul style="list-style-type: none"> – Simple control, operation, and maintenance – No electro-mechanical required 	<ul style="list-style-type: none"> – Huge land requirement – Odor problem – Groundwater contamination
(d) Duckweed pond system	<ul style="list-style-type: none"> – Proper covering prevents mosquito breeding and odor – Yield of proteinaceous material as animal feed 	<ul style="list-style-type: none"> – Low pathogen removal
(e) Facultative aerated lagoon	<ul style="list-style-type: none"> – Simple operation – Simple installation issue – Lower energy cost 	<ul style="list-style-type: none"> – Possibility of groundwater contamination
(f) Activated sludge treatment	<ul style="list-style-type: none"> – Less land requirement 	<ul style="list-style-type: none"> – Costly – Foam formation affects the process
(g) Biological, filtration, and oxygenated reactor technology	<ul style="list-style-type: none"> – Space saving – Odor-free – Less operational supervision 	<ul style="list-style-type: none"> – Sludge formation

11.4 Nanotechnology in Waste Management

Nowadays, nanotechnology is not only limited to sectors like energy (Luther 2008), food safety (Joseph and Morrison 2006; Rao et al. 2017a, b), electronics (Bhat 2007), agriculture (Joseph and Morrison 2006; Rao et al. 2017a, b; Sangeetha et al. 2017a, c), medicine (Nikalje 2015) rather has occupied a space in environmental protection and waste management is delineated in Fig. 11.3. Nanotechnology is compassionately involved with materials of dimensions ranging from 1–100 nm. The inducement for nanomaterial versatility and lessen volume required in application is mainly because of tiny size that frills enhanced reactivity for adsorption, catalysis of several contaminant groups such as organics, for example, polycyclic aromatic hydrocarbons (Yang et al. 2006), heavy metals like barium (Çelebi et al. 2007) and inorganics like nitrate (Joo and Cheng 2006).

Nanotechnology is definitely proven as a screen raiser at each stage of waste management that is PR3ED (prevention-reduction-reuse-recycle-energy recovery-disposal) and is briefly described as follows.

11.4.1 PR3ED

Nanomaterials credibly is a good replacer as in making the process greener by substituting materials that undergo high-energy consumption, curtailment of toxic chemicals, solvent thus enhancing manufacturing efficiency and so reduction of waste and pollution (Shan et al. 2009). According to Kumar et al. (2016), nanomaterials like fullerene and carbon nanotubes have superior mechanical and electronics properties that frame it as meritorious in various applications like field emission display, battery storage media, and nanoelectronic devices. They explained that use

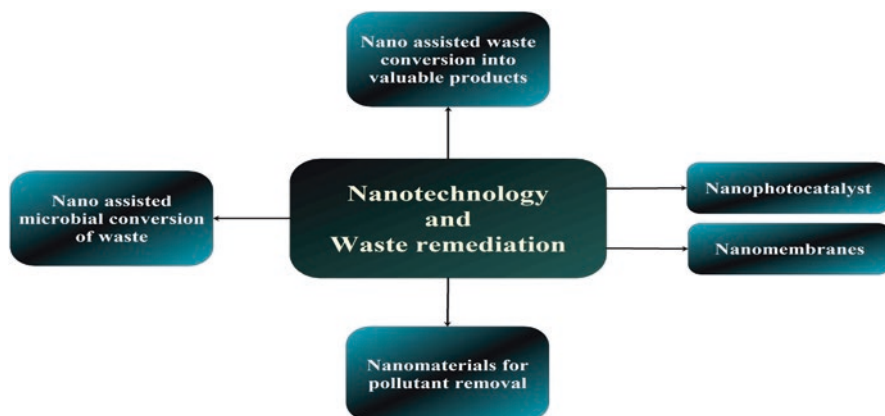


Fig. 11.3 Panoramic view of nanotechnology in waste remediation

of carbon nanotubes (p-type semiconductor) in solar cells enhances its absorption efficiency. Further, they concluded that multi-walled carbon nanotube absorbs additional power than single walled nanotube in the solar cells. In a research performed by Li et al. (2013), graphene and carbon nanotubes endowed as fetching material for photovoltaic system. These materials possess optical and electronic properties that propel its direct use for improving the energy conversion in thin film solar cells. Altaiaif et al. (2014) in their review explained that silicon-based solar cells are used at large scale but these cells possess major setback of not being cheaper. They considered organic material occupied solar cells as the potential candidate. They explained organic material to be the best alternative, as it possesses conducting as well as semi-conductive properties, low cost, simple manufacturing protocol, and high throughput. Above all goodness, organic solar cells power conversion efficiency elevates with increment in temperature in comparison to the inorganic solar cells, which decreases upon elevated temperature. Thus, nanomaterials are rather to be called as magic bullets at the pollution prevention stage, as being explained in the above examples.

Shan et al. (2009) in their review mentioned that nanocatalyst supplemented to diesel fuel helps in high efficient burning thus eventuate in release of fewer flue gases. Also explained that nanofabricated sorbents provide better adsorption of pollutants. To expunge CO₂ from smokestack nanocrystal proved to be effective. Nanocrystal works by conferring an electron to CO₂ to react with other molecules and making it non-toxic. They cited another example wherein functionalized sorbents are very effective for diminution of mercury, a pollutant transported globally from coal combustion. A couple of mercury removal sorbents like titanium oxide nanocrystal and iron oxide NPs were explained, where former one has to undergo maintenance periodically.

Reuse of materials after its implication to waste remediation subsist the third most favorable step in waste hierarchy. According to Lunge et al. (2014), magnetic NPs as such or bolstered adsorbents can be effortlessly reused after their separation through outwardly applied magnetic field. These NPs have become center of attraction for environmental remediation, as it owes high surface area and super paramagnetic properties. They reported that magnetic NPs could remove organic pollutants like phenols and dyes and ions like arsenic, mercury, nickel, copper, fluoride, chromium, etc. Group of scientist Tran et al. (2010) fabricated oxide magnetic NPs like magnetite, manganite, and spinel ferrite. Among them magnetite magnetic NPs were utilized for confiscation of heavy toxic metals like lead and arsenic from desecrated water. Recycling and energy recovery are the interlinked stages in waste hierarchy. Recycling is a protocol wherein waste materials either are converted to fresh usable material or object. Therefore, recycling contribute as in reduction of crude raw materials and appositeness of waste with potential of being useful. The role of a few nanomaterial-assisted waste conversion is mentioned in Table 11.3.

The least favorable step in the waste pyramid is disposal. According to Shan et al. (2009), incineration of waste for its disposal possess many advantages like complete destruction, reduction in usage of land, and aids in energy recovery too. However, incineration can impose environmental issues like emission of dioxin

Table 11.3 Catalogue of nanomaterial-assisted waste conversion

Waste source	Waste-treated		References
	Nanomaterial	Other	
Waste cooking oil	Mesoporous silica/ superparamagnetic iron oxide core shell NPs	Lipase enzyme	Karimi et al. (2013)
Olive mill wastewater	Titanium(IV) oxide anatase, iron (III) oxide nanorods NPs	Fungi	Nogueira et al. (2015)
Waste cooking oil	Magnetic NPs	Lipase enzyme	Yu et al. (2013)
Rice husk	Calcium hydroxyapatite NPs	Cellulose and xylanase	Dutta et al. (2014)
Water with high phosphate content	Iron NPs	Spondias purpurea seed waste	Arshadi et al. (2015)
Waste cooking oil	Molybdenum oxide/Zirconia NPs	Ferric manganese	Alhassan et al. (2015)
Organic pollutant	Nitrogen-doped carbon nanotube	Iron	Yao et al. (2017)

from incineration process. They reported in their review about the coalition disposal by employing incineration and nanophotocatalyst. The list of few nanophotocatalyst for environmental pollutants removal mentioned in the research article of Shan and co-researcher is mentioned in Fig. 11.4.

The fact is plastics are not biodegradable due to inertness of material it is being made of. Fa et al. (2011) came up with an approach to make plastics degradable by embedding functionalized TiO₂ NPs into commercial poly(vinyl) chloride (PVC). The TiO₂ NPs were modified with perchlorinated phthalocyanine iron (II) (TP) to embellish their photocatalytic task. It was illustrated that the TP composite degradation efficiency was incomparably elevated under UV and sunlight luminosity than the primeval PVC and the composite PVCTiO₂. Table 11.4 comprises of list of nanomaterials knotted in environmental pollutants remediation (Shan et al. 2009; Gangadhar et al. 2012; Wang et al. 2012a, b; Amin et al. 2014).

11.5 Trash: Repository of Nanomaterial

11.5.1 Nanomaterial from Garbage

Garbage is the unpretentious materials discarded by human beings excluding toxic waste products. It includes kitchen or food items like poultry/slaughterhouse waste. The following tract deals with the repository of nanomaterial in garbage.

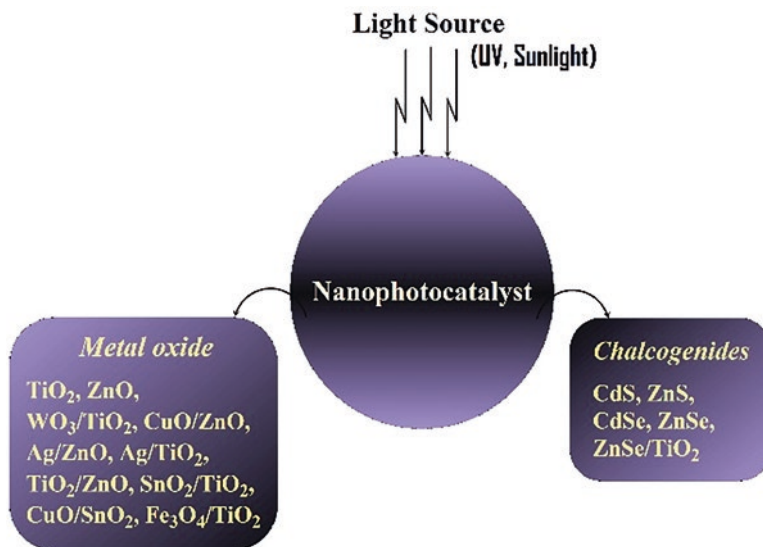


Fig. 11.4 Nanophotocatalyst for environmental pollutants removal

11.5.1.1 Kitchen Waste

Everyday our kitchen generates lots of biodegradable green waste. It primarily comprises of fruit and vegetable peels. These waste peels are abounded in metabolites that have the potential to achieve nanoconversion. *Lansium domesticum* peels, a fruit with a common name as longkong carries plenteous metabolites like terpenoids (lansionic acid, triterpene glycosides) and organic compounds (lansionic acid and methyl ester), accomplish reduction of metal ions to stable NPs by capping it. These metabolites possess strong reducing potential (Shankar et al. 2014). Likewise, pomegranate peels are enriched with polyphenols like condensed tannins, hydrolysable tannins, ellagic and gallic acids (Goudarzi et al. 2016). According to Kuppusamy et al. (2015), polyphenols are the superior candidate for green NPs fabrication due to following betterment (a) non-toxic, (b) control the size, morphology of NPs, (c) simple synthesis mechanisms, (d) can be scaled up with minimum cost, (e) environmental friendly. They explained the three-fold working of polyphenol mediated NPs formation as polyphenol complex formation is the first step, followed by bioreduction of metal ion to nascent ion, and finally capping of fabricated NPs by phenolics (oxidized).

Other peels like papaya are loaded in metabolites like chymopapain and papain (Kokila et al. 2016), mango peel is endowed with polysaccharides, lignins, flavonoids, hemicelluloses, and pectins (Yang and Li 2013), Orange peels loaded with limonene, citral, neohesperidin, naringin, rutin, rhamnose, eriocitrin, and vitamin C (Rao et al. 2017a). Banana peels are bloated with polymers like lignins, hemicelluloses, and pectins (Bankar et al. 2010) and watermelon rind comprises of metabolites like cellulose, citrulline, pectins, proteins, and carotenoids (Patra et al. 2016).

Table 11.4 List of nanomaterial/nanoparticles mediated environmental pollutants remediation

Nanomaterials	Environmental pollutants
Lead, nickel, zinc, copper	Alumina
Radioactive metal toxin	Biophosphonate-modified magnetite
Polycyclic aromatic hydrocarbon, trihalomethanes, atrazine, lead, cadmium, chromium, zinc, polycyclic aromatic compound, chlorophenols, herbicides, dichlorodiphenyltrichloroethane	Carbon nanotube
Copper, lead, cadmium, zinc	Carbon nanotube/hydroxyquinoline
Crocein orange G, acid green 25	Chitosan-based Fe ₃ O ₄
Cyanine acid blue	Copper/iron oxide sawdust
Arsenic, chromium	Cerium oxide
Arsenic	Cerium oxide supported carbon nanotube
Arsenic and chromium	Flower-like iron oxide nanostructure
Cadmium, cobalt	Graphene nanosheets
Acid black 24, nitrate, barium, humic acid, arsenic, cadmium, chromium, nickel, lead, nitrate, perchlorate, organic compounds, 2,2' dichlorobiphenyl	Iron oxide
Phosphate	Iron/granular-activated carbon
Chromium	Iron oxide coated polypyrrole
Arsenic	Magnetite/graphene
Nickel	Magnesium hydroxide/alumina nanocomposite membrane
Organic dyes	Manganese oxide films
Nickel	Magnesium oxide/nickel oxide/alumina
Toluene, benzene	Multi-walled carbon nanotubes/iron
Acid green 27	Nanochitosan
Nickel	Nanocrystalline calcium hydroxyapatite
Benzene, toluene, xylene, ethylbenzene	Nanoporous-activated carbon fiber
Azo dyes and phenols	Nitrogen- and iron-doped titanium dioxide
Chromium	Palladium
Nitrate	Palladium/copper/alumina
Trichloroethylene	Palladium, palladium/gold
Heavy metals	Polyrhodamine magnetic
Copper, lead	Polylayered silicate nanocomposite

(continued)

Table 11.4 (continued)

Nanomaterials	Environmental pollutants
Organic dyes	Silver/amidoxime fiber
4 nitrophenol	Sulfate ion/titanium dioxide
Acid orange 7, reactive orange 16, polychlorinated biphenyls, benzene, chlorinated alkanes	Titanium dioxide
Malachite green	Tin-doped titanium dioxide double layer thin films
Cadmium	Titanate nanoflowers
Arsenic	Titanium dioxide/magnetite
Chromium	Titanium dioxide/graphene sheet
Polychlorinated biphenyls, benzene, chlorinated alkanes	Titanium dioxide
Total organic content	Titanium dioxide and alumina
Toluene	Titanium nanorods
4- chlorocatechol	Zinc oxide
Thiophene	Zinc-based nanocrystalline aluminum oxide (Zn/Al ₂ O ₃)

Table 11.5 Fraction of consumed non-vegetarian food from the source

Non-vegetarian (Jha and Prasad 2016)	
Animals (each)	% Utilization
Cow	50–54
Sheep/goat	52
Pig	60–62
Chicken	68–72
Turkey	78

11.5.1.2 Poultry and Slaughters Waste

Not anyone in the world will deny possessing food drive we all drool towards yummy food with the choice to plum on plant based or animal food. However, the point is to bring into the limelight about the food processing waste generated in tons globally. This section ratifies poultry and slaughterhouse waste and their possible exorcism. Animal food subsumes both edible and non-edible parts (choice-based). Table 11.5 illustrate fraction of food that is only consumed. From production to processing, slaughter house and poultry procreate refusals like hatchery waste, sawdust, wood shavings, straws, peanuts, feathers, entrails, organs of murdered birds, processing wastewater, bio-solids, blood, hides, bones, and most of these are constructed with organic and inorganic nutrients. The above consequences diminish the essence of water, soil, and air as well (Williams 2008). A few options like

applicability of poultry waste by-products to land application as crop nutrients, animal re-feeding, and biogas production from slaughterhouse waste were implemented to discern the natural terrain (Williams 2008; Ek et al. 2011; Ahmad and Ansari 2012; Malav et al. 2018). A group of experimenter propounded a safe method to decompose broiler slaughterhouse waste verging on to coir pith together with caged layer manure from poultry farms (Bharathy et al. 2012). Another major concern is the increasing population, as will impose hefty demand on the devastation of poultry and animal meat and inasmuch the waste generation. Therefore, dependency wholly on the above-mentioned management techniques would not rather be effective. From ended few years, researchers are putting effort to harness NPs from poultry-cum-slaughters waste pauperizing the load on other management modes.

11.5.1.3 Chicken Offals

11.5.1.3.1 Eggshells

A couple of researchers passed on a neoteric approach to use waste eggshells as such serving as a reactor system for controlled synthesis of amorphous $\text{Co}(\text{OH})_2$ nanorod arrays accompanying on Ni foam, Ti foam, or glass as substrate and also swept off the fact of not being synthesized conventionally by direct mixing of the parent constituents. The metabolism of embryo creates carbonate ions, upon reaction with calcium ions coming out of uterus step up to sturdy, protective eggshell. They have utilized CoSO_4 and NaOH solution, the former one withheld in the emptied eggshell and the later one outside the shell. Being porous in nature, bestowed protein membrane is permeable and thus permitting the diffusion of ions slowly is definitely a stringent condition to procure $\text{Co}(\text{OH})_2$ nanorods (Meng and Deng (2017)). Natural offal-like eggshell implied to be quite promising for manipulating materials at nanoscale. In another work, group of experimenters reported calcium carbonate nanoparticles fabrication using waste eggshells, majorly sourced to have 94% of calcite and other components. Figure 11.5 portrays various components present in eggshell. They achieved nanosize by virtue of mechanochemical cum sonochemical method, ball milled precisely in wet condition (polypropylene glycol) to avoid iron contamination through steel and superseded with high intensity ultrasonic horn in propinquity of N,N-dimethylformamide (DMF), decalin, and tetrahydrofuran. An irregular, 10 nm sized CaCO_3 NPs were established after characterization (Hassan et al. 2013). According to Wang et al. (2012a, b), microwave-assisted concept was operated to contrive fluorescent and water soluble C-Dots due to efficient and intensive energy treatment by microwave. They have devised a green, rapid, and eco-friendly method to fabricate C-Dot from easily procured protein-rich eggshell membrane trash that showed excellent fluorescent property detected by photoluminescence emission spectra.

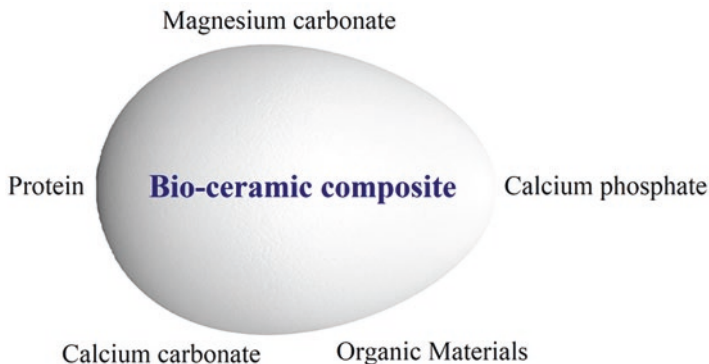


Fig. 11.5 Components of eggshell convoluted in nanotransformation

Fig. 11.6 Pictorial representation of constituents of feather



11.5.1.3.2 Feather

Poultry processing plants not only serves us with flesh but also creates heap of feathers each year. Sundaram et al. (2015) demonstrated green synthesis of keratin NPs from chicken feather. In addition, they studied morphology of designed keratin NPs by scanning electron microscope and X-Ray diffraction. Feathers are protein rich. Figure 11.6 represents the constituent elements of feathers. In cosmetic products, keratins are primarily used. In another work, Gao et al. (2014) developed a strategy to perform pyrolysis of chicken feather offal to Ni₃S₂-carbon coaxial nanofiber, in the subsistence of the catalyst nickel acetate tetrahydrate at 650 °C. The product then acidified to obtain nitrogen-doped carbon nanotube. They reported 41.8% chicken feather carbon conversion to N-CNT and confirmed via characterization through FE-SEM, TEM, XPS, and XRD.

11.5.1.3.3 Fish Offal

Jha and Prasad (2014) accounted a new technique to cut down fish discard in stipulation to fabricate nanomaterial to overcome dirtiness. Fish discard from kitchen and fish market are comparatively quite lesser than coastal processing sector. These are propertied with highly complex molecules (proteins) and essential fatty acids. They

made it happen, as combo of an aggregates and individual silver NPs were fabricated ranging from 8 to 40 nm from gut waste of the fish (*Labeo rohita*) and were further characterized for confirmation. They proposed a mechanism of silver NPs biosynthesis from fish discard extract and summarized in Schematics (Fig. 11.7a).

In an another investigation on fish discards, a couple of researcher utilized the potential of fish scales of *Labeo rohita* for fabrication of copper NPs (25–37 nm) with no outsourced stabilizing and reducing materials. They also contemplated the mechanism for the fabricated copper NPs, outlined in Schematics (Fig. 11.7b) (Sinha and Ahmaruzzaman 2015).

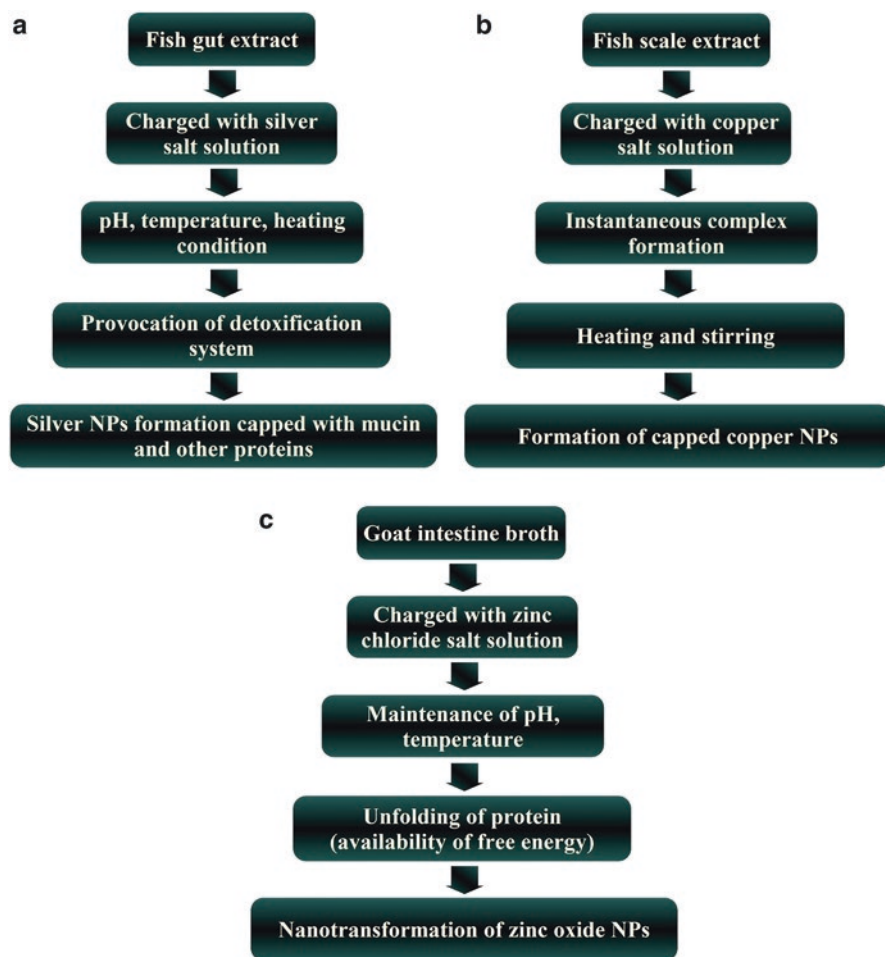


Fig. 11.7 (a) Contemplated mechanism of silver NPs from fish *Labeo rohita* gut. (b) Contemplated mechanism of Cu NPs fabrication from scales of fish *Labeo rohita*. (c) Contemplated mechanism of zinc oxide NPs fabricated from goat intestine

11.5.1.3.4 Goat Offal

In a study, goat intestine waste was utilized for the artifact of zinc oxide NPs through green, eco-friendly protocol in a concern to intercept environmental pollution. The particle size of zinc oxide NPs fabricated were in the range of 3–11 nm. Employing UV-visible spectroscopic technique, complete reaction decorum was monitored. A contemplated mechanism for biological synthesis of zinc oxide NPs has been proffered and is summarized in the Schematics (Fig. 11.7c) (Jha and Prasad 2016).

Chamundeeswari et al. (2011) reported the artifact of magnetic iron NPs from goat blood by incineration method. In her another experimental work, she applied a simple wet-precipitation mode to fabricate another nanobiocomposite employing the iron NPs with different coating material (collagen) (Chamundeeswari et al. 2013a). Further, she extended her work to fabricate bionanocomposite using iron NPs with a mixture of chitosan and gelatin with varying size that ranges from 80 to 300 nm. The so-formed material possesses magnetic properties having magnetic saturation of 18.97 emu/g (Chamundeeswari et al. 2013b).

11.5.2 *Nanomaterials from Combustible Waste*

Literally, combustion is a phenomena wherein burning occurs by virtue of the reaction between the reductant and an oxidant to exonerate light and heat. The material that bear up combustion are expounded as combustible material and so as combustible waste are defined. On the basis of origin, combustible waste could be either of two types (a) natural combustible waste (NCW) and (b) synthetic combustible waste (SCW). NCW comprises of fallen leaves, waste paper, wood, bagasse, etc., wherein SCW includes cigarette butt, diapers, plastic bottles, ceramics, porcelain, rubber, leather, clothes, etc. Numberless researchers have taken effort to utilize specified combustible waste to value-added products as nanomaterials (Table 11.6). Researchers have fabricated nanomaterials through green, chemical and physical protocol. They synthesized graphene from various combustible wastes (Akhavan et al. 2014; Suryawanshi et al. 2012; Adolfsson et al. 2015; Gong et al. 2014; Sharma et al. 2014; Essawy et al. 2017).

Akhavan et al. (2014) explained in their work about the fabrication of graphene from cheap progenitor source like bagasse, wood, leaf, fruit waste, bone, cow dung, and newspaper through chemical method. They worked to conquer the limitation of using notably pure graphite as the initial source for fabrication. The sources they have chosen are well provided in carbon content. The graphene sheets they have synthesized were exclusive of the initial material and purity was propped similar to the graphene sheets obtained through Hummers' method.

Another group of investigators employed carbon source as spent neem leaves to fabricate graphene quantum dots. The dried neem leaves were submitted to pyrolysis to procure black powder, and further ball milled to obtain fine powder. The so-obtained ball milled powder considered as precursor for graphene quantum dots

Table 11.6 Catalogue of trash sourced nanomaterials

Waste sources	Concerned nanomaterial	Synthesis approach	References
<i>Kitchen waste</i>			
Banana peel	Silver NPs	Bioinspired	Bankar et al. (2010)
Orange peel	Silver NPs	Biosynthesis	Kaviya et al. (2011)
<i>Punica granatum</i> peel	Silver NPs Gold NPs	Biosynthesis	Ahmad et al. (2012)
<i>Punica granatum</i> peel	Silver NPs	Biogenesis	Edison and Sethuraman (2013)
Mango peel	Silver NPs	Green synthesis	Yang and Li (2013)
Orange peel	Silver NPs Platinum NPs	Biosynthesis	Castro et al. (2015)
Food waste	Carbon nanodot	Ultrasound irradiation	Park et al. (2014)
<i>Lansium domesticum</i> fruit peel	Gold NPs	Green synthesis	Shankar et al. (2014)
<i>Rambutan</i> peel	Zinc oxide nanocrystals	Green synthesis	Yuvakkumar et al. (2014)
Banana peel	Silver NPs	Biosynthesis	Ibrahim (2015)
Cavendish banana peel	Silver NPs	Biological	Kokila et al. (2015)
Vegetable waste	Silver NPs	Green synthesis	Kumar et al. (2015)
<i>Citrullus lantus</i> rind	Gold NPs	Biosynthesis	Patra and Baek (2015)
Waste vegetable peel	Silver NPs	Green synthesis	Sharma et al. (2016)
<i>Arachis hypogaea</i>	Silver NPs	Green synthesis	Velu et al. (2015)
<i>Citrus sinensis</i>	Carbon NPs	Green synthesis	Adedokun et al. (2016)
Pomegranate peel	Silver NPs	Facile thermal decomposition	Goudarzi et al. (2016)
<i>Carica papaya</i> peel	Silver NPs	Green synthesis	Kokila et al. (2016)
Banana peel extract	Silver NPs	Green synthesis	Narayanamma et al. (2016)
Rind of watermelon	Silver NPs	Biosynthesis	Patra et al. (2016)
Mangosteen pericarp waste	Silver NPs Gold NPs	Green synthesis	Park et al. (2017)
Orange peel	Carbon dots	Hydrothermal carbonization	Prasannan and Imae (2013)
Orange peel	Silver NPs	Biogenesis	Rao et al. (2017a)
Orange peel	Silver NPs	Biosynthesis	Saratale et al. (2017)
<i>Poultry and slaughters waste</i>			
Goat blood	Iron NPs	Incineration	Chamundeeswari et al. (2011)
Eggshells membrane	Carbon nanodots	Microwave-assisted	Wang et al. (2012a, b)
Goat blood	Iron NPs coated with collagen	Wet-precipitation	Chamundeeswari et al. (2013a)

(continued)

Table 11.6 (continued)

Waste sources	Concerned nanomaterial	Synthesis approach	References
Goat blood	Iron NPs coated chitosan and folic acid	Incineration	Chamundeeswari et al. (2013b)
Eggshells	Calcium carbonate NPs	Mechanochemical cum sonochemical	Hassan et al. (2013)
Chicken feather (including quills and barbs)	Nitrogen- doped carbon nanotubes	Biological synthetic protocol	Gao et al. (2014)
Gut of fish <i>Labeo rohita</i>	Silver NPs	Biological synthetic protocol	Jha and Prasad (2014)
Fish scales of <i>Labeo rohita</i>	Copper NPs	Green protocol	Sinha and Ahmaruzzaman (2015)
Chicken feathers	Keratin NPs	Biological synthetic protocol	Sundaram et al. (2015)
Goat slaughters waste (intestine)	Zinc oxide NPs	Biological synthetic protocol	Jha and Prasad (2016)
Ferrocene-chicken oil mixture	Vertically aligned carbon nanotube	Thermal chemical vapor deposition	Suriani et al. (2016)
Eggshells	Cobalt hydroxide NPs	Bioinspired	Meng and Deng (2017)
<i>Combustible waste</i>			
Wood wool	Carbon nano-onions	Pyrolysis	Sonkar et al. (2012)
Wood, leaf, bagasse, newspaper, soot powder	Graphene	Chemical method	Akhavan et al. (2014)
Fallen willow leaves	Carbon nanosphere	Thermal decomposition	Qu et al. (2014)
Dead neem leaves	Graphene quantum dots	Pyrolysis	Suryawanshi et al. (2012)
Mineral water bottles(used)	Nanocarbon tube	Arc-discharge method	Berkmans et al. (2014)
Waste polypropylene	Graphene flakes	Pyrolysis	Gong et al. (2014)
Tyre rubber	Silicon carbide NPs	Pyrolysis	Rajarao et al. (2014)
Solid waste plastic	Graphene crystals	Pyrolysis	Sharma et al. (2014)
Waste paper	Graphene oxide quantum dots	Microwave-assisted thermal degradation/sonication	Adolfsson et al. (2015)
Corrugated container	Cellulose nanocrystal	Enzymatic hydrolysis and sonication	Tang et al. (2015)

(continued)

Table 11.6 (continued)

Waste sources	Concerned nanomaterial	Synthesis approach	References
Polyethylene terephthalate bottle waste	Graphene	Thermal decomposition	Essawy et al. (2017)
Cigarette butt	Silver nanostructure	Green protocol	Murugan et al. (2017)
Lard oil	Graphene sheets	Inductively coupled plasma-assisted chemical vapor deposition	Wu et al. (2017)
<i>Ashes</i>			
Coal fly ash	Carbon nanofiber	Catalytic chemical vapor deposition	Hintsho et al. (2014)
Coal fly ash	Carbon nanomaterial	Catalytic chemical vapor deposition	Hintsho et al. (2016)
Pure rice husk ash	Nanosilica	Precipitation	Sinyoung et al. (2017)
<i>Waste microorganisms</i>			
Bacteria	Lithium metal phosphate NPs	Biological	Zhou et al. (2014)
Bacterial cellulose	3D carbon nanomaterials	Pyrolysis	Wu et al. (2016)
Metarhizium robertsii	Silver NPs	Photo-induced biosynthesis	Rożalska et al. (2016)
<i>Pharmaceutical waste</i>			
Norfloxacin tinidazole combination	Gold, zirconia oxide, cadmium sulfide	Green protocol	Jha and Prasad (2012)
<i>Agricultural waste</i>			
<i>Avena sativa</i> biomass	Gold NPs	Green protocol	Armendariz et al. (2004)
<i>Annona squamosa</i> peel	Silver NPs	Green protocol	Kumar et al. (2012)
Coconut shell	Porous graphene nanosheet	Simultaneous activation-graphitization	Sun et al. (2013)
Cotton wood	Magnetic biochar	Pyrolysis	Zhang et al. (2013)
<i>Punica granatum</i> peel	Platinum NPs	Green protocol	Dauthal and Mukhopadhyay (2014)
Grape stem, stalk, seeds	Gold NPs	Green protocol	Krishnaswamy et al. (2014)
Oil palm leaves	Porous carbon NPs	Pyrolysis	Kumar et al. (2014)
Rice bran	Gold NPs	Green protocol	Malhotra et al. (2014)
Waste cotton	Cellulose NPs	Green method	Meyabadi et al. (2014)
Sugarcane bagasse	Graphene oxide	Muffled atmosphere	Somanathan et al. (2015)

(continued)

Table 11.6 (continued)

Waste sources	Concerned nanomaterial	Synthesis approach	References
Bilberry waste, spent coffee grounds	Silver NPs	Green protocol	Baiocco et al. (2016)
Coffee silverskin	Lipid NPs	Homogenization/sonication	Rodrigues et al. (2016)
Bagasse	Magnetic biochar	Pyrolysis	Thines et al. (2017)

fabrication. Upon diluting the precursor with water, mixture was dispensed to filtration to disarticulate the unreacted carbon and the bulkier particles. The filtrate showed strong fluorescence thus resembling graphene quantum dots (Suryawanshi et al. 2012). Similarly, through pyrolysis Gong et al. (2014), Rajarao et al. (2014) and Sharma et al. (2014) harnessed the potential of waste polypropylene, tyre rubber, solid waste plastic, wood wool to procure graphene flakes, silicon carbide NPs, graphene crystal, carbide nano-onions, respectively.

Through microwave-assisted thermal degradation coupled with sonication to procure graphene oxide quantum dots were taken up by Adolfsson et al. (2015). They fabricated nanomaterial from cellulose through the embodiment of an intermediate as carbon nanosphere. Upon degradation of catalyst by means of H_2SO_4 carbon nanosphere is obtained. Further, the intermediate were sonicated and heated in the aura of HNO_3 to stockpile graphene oxide quantum dots.

Murugan et al. (2017) worked on green protocol to fabricate silver NPs using cigarette butt waste. Cigarette butt comprises of polycyclic aromatic compounds, heavy metals nicotine, and ethyl phenol. They prepared two different extracts with and without tobacco. The varying extracts were charged with silver nitrate salt solution under the reaction conditions. Further, the fabricated silver NPs were characterized.

In the majority of research work, mechanism of creation of NPs from agricultural waste is not revealed. Malhotra et al. (2014) in their study investigated the mechanism involved in biomineralization of gold NPs from rice agro-waste (rice bran). They deciphered that ferulic acid, as the function molecule is accountable for the bioconversion gold salt to gold metal. They also monitored the heat modification in the bioconversion process and concluded the process to be exothermic in nature. The reaction between the ferulic acid and the gold salt was of first-order kinetics.

11.5.3 Nanomaterials from Ash

Thermal power plant produces offshoot as fly ash upon ignition of coal. Fly ash is removed from combustible gases before being set free into the surroundings. The morphological feature of fly ash is spherical with diameter ranging from 1 to 150 μm . The chemical makeup of fly ash depends upon the nonexplosive matter in

the coal (Ramezaniapour 2014). Hintsho et al. (2016) that out of 800 million tons of coal fly ash only 15% are being recycled have reported it. Recyclability of fly ash surely is the fruitful outcome as they stated about its high disposal cost and as an environmental threat. They also explained its present applications (mine fill, mine site remediation, adsorbent for heavy metals, catalyst), with none of them commercially being employed. In this background, nanotechnology is at budding stage to unburden the tons of fly ash load aids in creating pollution.

According to Sinyoung et al. (2017), nanosilica is created through established method from sodium silicate upon heating sodium carbonate with quartz at very high temperature (1300 °C). High-energy requirement made this process a bit costlier. Therefore, to overcome this cost issue nanosilica produced from rice husk ash is advantageous, apart from cost it also lower the risk imposed on the environment pollution. They also explained the groundwork of nanosilica (5–60 nm) from rice husk ash having porous structure. The nanosilica was calcined in the laboratory to decontaminate K_2O , CaO , and MgO .

In another abstraction, carbonaceous nanostructures were fabricated from South African fly ash. Fly ash is a waste product consummated from the thermogenesis of coal, and its constituents were found to be Al_2O_3 , SiO_2 , FeO , Fe_2O_3 , MnO , MgO , Na_2O , CaO , and K_2O after examining it through X-ray diffraction. Above all, it acts as catalyst for the proliferation of carbon nanomaterials. The carbon nanofibers were fabricated through catalytic chemical vapor deposition method in shade of acetylene gas extremely elevated temperature (400–700 °C). Further carbonaceous were characterized by transmission electron microscopy, laser Raman spectroscopy, Brunauer–Emmett–Teller analysis to measure surface area, and thermogravimetric analysis to quantify carbon content (Hintsho et al. 2014).

Hintsho et al. (2016) in their research article studied about the gaseous (nitrogen and hydrogen) significance on the assembly of carbonaceous nanomaterials from acetylene in the presence of fly ash catalysts. They came up with the matter that hydrogen gas procured higher yield of carbonaceous nanomaterial than nitrogen, reasoned by virtue of the multifunctional roles of hydrogen. Further, the materials formed were featured by the methods like Raman spectroscopy and Mössbauer spectroscopy.

11.5.4 Nanomaterials from Pharmaceutical Waste

Pharmaceutical waste is consolidated outcome of expired medicines/products, contaminated drugs, and discarded/unused chemicals. Figure 11.8 represents various progenitors of pharmaceuticals that aids in enhancing environment pollution. Not much research work has been absorbed in this area, so nanomaterials fabrication could be a more desirable option for pharma companies to recycle leftover medicines.

According to Kadam et al. (2016), only the functioning part of the engulfed pharmaceuticals is metabolized by the biological system of ours and the non-metabolized



Fig. 11.8 Representation of major progenitor of pharmaceutical waste that pollutes environment

part enters the environment through excretions. The final terminus of excrete is lakes and other natural water sources. They documented that health center generates approximately 40,000 tons of waste per day in India.

Jha and Prasad (2012) in their unique research work opened up a pathway to recycle waste drugs to fabricate nanomaterials like metal (gold), oxide (zirconia oxide), and chalcogenide (cadmium sulfide) NPs. This proposal could be a boon to pharma companies in recycling waste as they have implemented green protocol to achieve nanosynthesis. They utilized quinolone group of antibiotic (norfloxacin) and tinidazole combination to fabricate above-mentioned nanomaterials. They prepared reaction broth utilizing 4 month expired Norflox-TZ dissolved initially in sterile distilled water. Further, HCl was added to achieve complete dissolution of the tablet, and the mixture was heated over steam bath at 40 °C. The prepared broth was utilized for NPs fabrication. They explained molecular structure of compounds norfloxacin and tinidazole facilitates redox reaction. The ketonic group and fluorine atom in norfloxacin indicates redox potential (Fig. 11.9). The zwitterionic form of norfloxacin makes it a suitable candidate for nanosynthesis. The cationic form upon addition of metal ions generates oxide/chalcogenides NPs wherein the anionic form upon reaction with metal ion produces metal NPs.

11.5.5 Nanomaterials from Waste Microorganisms

Microbes are not only meant to cause diseases rather are of prime importance, carried from industrial importance to health insurance to environmental concern and many more. Undoubtedly, microbes work very well for us as antagonist and protagonist as well. In this section, a brief description about the utilization of waste biomass to nanomaterial genesis is focused, as its disposal is definitely a huge concern. Only limited research work has been taken up by the researcher.

Rożalska et al. (2016) fabricated silver NPs from *Metarhizium robertsii* (filamentous fungi) biomass after being employed for decontamination of nonylphenol. They have used multiple biomass extract dilutions to synthesize photo-induced silver NPs, wherein obtained better results with 20 and 50% diluted sourced samples

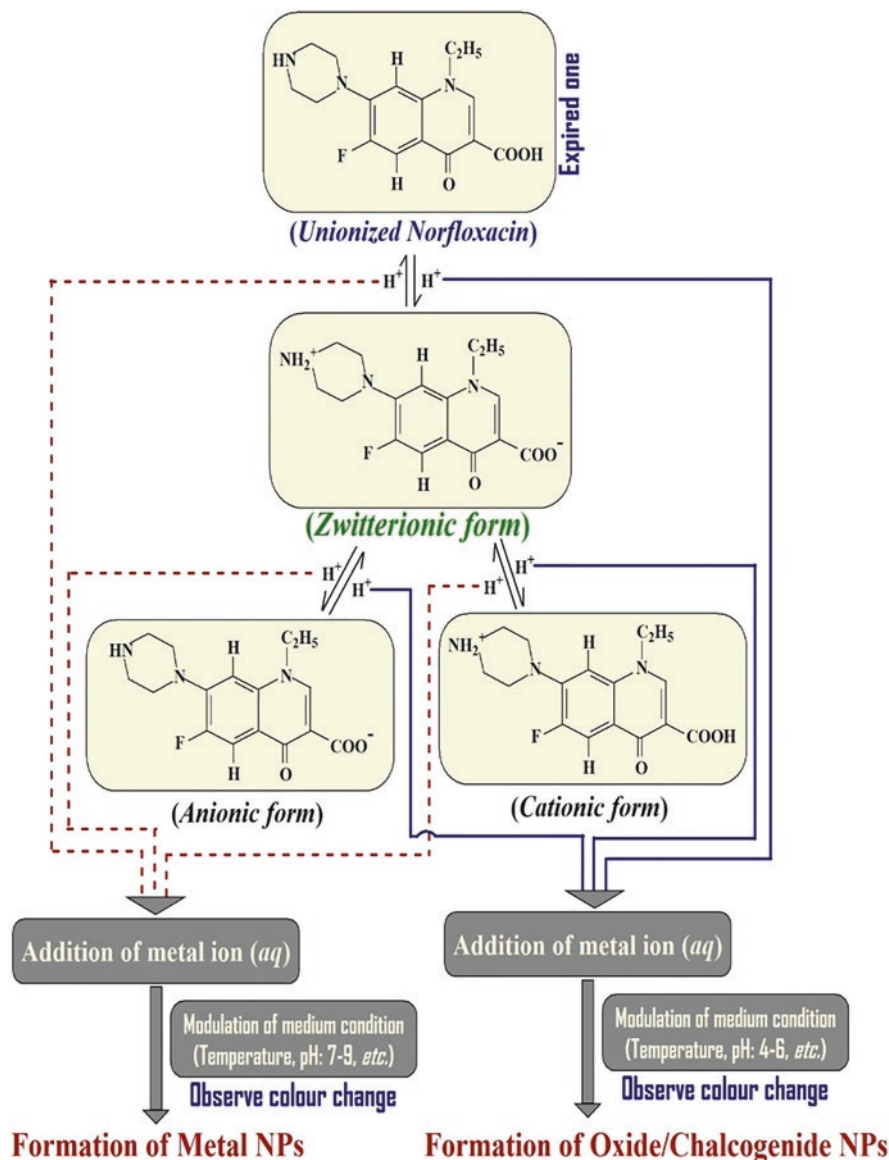


Fig. 11.9 Representation of zwitterionic form of expired norfloxacin and formation of metal and oxide/chalcogenide NPs upon addition of metal ions

within 3 h. The so-obtained nanomaterials were homogeneous in size and shape after being characterized by UV-Visible spectrophotometer, FT-IR, TGA, XPS spectroscopy, STEM, and DLS. FT-IR and XPS analysis confirmed the involvement

of protein in the nanofabrication and further capping agents were quantified by thermogravimetric analyses.

Another group of researcher demonstrated the conversion of polyphosphate accumulated rich recombinant *E.coli* and wild type *E.coli* into lithium monophosphate nanostructure. Initially, the two categories of cells were harvested from phosphate-rich media with 20 percent more media depleted by recombinant strain. Further cells were treated with metal ions (FeCl_3) followed by lithium acetate solution and then annealed at 600 °C. Nanostructures formed were characterized by XRD, TEM, and EDX. TGA analysis reveals 20 wt% carbon content derived from the bacteria (Zhou et al. 2014).

Wu et al. (2016) mentioned in their article about bacterial cellulose, a biomass matter and its conversion to high value-added three-dimensional carbon nanomaterials. Bacterial cellulose is a three-dimensional nanoporous cellulose network that makes it an effective reaction system. They accounted on preparation of various nanomaterials like CNF aerogels.

11.5.6 Nanomaterials from Agricultural Waste

Agricultural wastes are generally the remainder of agricultural whirl. It comprises of crop residue, peels, pulp, stem, stalk, seeds, leaves, bagasse, fertilizers, and manures. Zhang et al. (2012) characterized agricultural waste based on the following five criteria: (a) Energy content of the waste (fruit waste), (b) Biomass combustion (grassland fires, crop residue burning forest), (c) Agricultural and natural fibers (cereals/insoluble fiber residue), (d) Bacterial and fungal communities (grown over the leftovers), (e) Decomposition (fruits and vegetables), (f) Agricultural water pollution (fertilizer/manure) (Sangeetha et al. 2017a, b, c). With increasing population, there is high demand on the food and so as the increment in agricultural waste (Sangeetha et al. 2017c). According to Castro et al. (2015), plant broths are economically useful for fabricating NPs following “green chemistry” approach with an additional advantage of undergoing scale up of the designed process. They elucidated that plant extracts endowed with biomolecules like enzymes, proteins, carbohydrates, organic acids, and amino acids, participate in NPs formation with dual function as reducing and capping negotiator is environmentally safe (Prasad 2014). Many researchers have taken effort to fabricate NPs from agricultural waste (Table 11.6) through green method, pyrolysis.

According to Dauthal and Mukhopadhyay (2014), agro-industrial waste *Punica granatum* peels effectively aided in fabricating platinum NPs. They elucidated that these peels are rich in ellagic tannins, ellagic acid, quercetin, gallic acid, punicalagin and endowed with antimutagenic, chemo-preventive, and antioxidant potential. They followed green protocol to fabricate platinum NPs through charging the extract by platinum salt solution under defined reaction conditions. Further, biofabricated platinum NPs was characterized. Armendariz et al. (2004), Kumar et al.

(2012), Krishnaswamy et al. (2014), Malhotra et al. (2014), Meyabadi et al. (2014), and Baiocco et al. (2016) also followed green protocol to fabricate NPs.

Zhang et al. (2013) fabricated magnetic/c-Fe₂O₃ composite through pyrolysis from cottonwood (pre-treated with FeCl₃). The biomass was kept in the FeCl₃ solution for couple of hours then air dried for 2 h at 80 °C. The prepared biomass was pyrolyzed in a furnace at particular reaction condition. Then, the composite procured were crushed and sieved accordingly.

Sun et al. (2013) for the first time fabricated graphene nanosheets from agricultural biomass waste coconut shell. They elucidated that coconut shell as a promising carbon source to fabricate activated carbon as these shells are enriched mainly with cellulose fibers. Above all coconut shells are cheap, environmental friendly, easily available in abundant quantity and most importantly a sustainable source. In the study, they have fabricated porous graphene-like nanosheets through effective simultaneous activation-graphitization route. The concept they employed is the synchronous ingress of the catalyst required for graphitization (FeCl₃) and activation (ZnCl₂) in coalition with the carbon source with metal precursor. They explained that after carbonization. They illustrated that the catalyst can form carburized phase during the heating process followed by fabrication of graphene-like nanosheets through organization cum disintegration phenomena of carburized phase. Finally, Fe components were discarded leaving behind the pure graphene-like nanosheets. Table 11.6 summarizes the synthesis of different nanomaterials synthesized from various waste sources.

11.6 Application of Nanomaterials Recycled from Waste

Nanomaterials procured from various waste sources are already revealed in the chapter. The comprehensive view of the applications of WMNPs has been elucidated below.

Zhang et al. (2013) prepared magnetic biochar and found its potential in arsenic removal. In addition, platinum NPs as a green catalyst for removal of pollutant like 3 nitrophenol in association with NaBH₄ were reported by Dauthal and Mukhopadhyay (2014). In another experimentation, silver NPs and nitrogen-doped carbon nanoparticle acts as catalyst to remove 4- nitrophenol (Edison and Sethuraman 2013; Gao et al. 2014; Rożalska et al. 2016). Further researchers have employed copper NPs, fluorescent carbon NPs to remove pollutant methylene blue dye (Sinha and Ahmaruzzaman (2015); Adedokun et al. 2016). Essawy et al. (2017) demonstrated removal of methylene blue and acid blue 25 by graphene NPs. Using carbon nanospheres, Rhodamine B and heavy metals were removed (Qu et al. 2014).

Biological applications of WMNPs include antibacterial (Kaviya et al. 2011; Yuvakkumar et al. (2014); Ibrahim 2015; Kokila et al. 2015; Patra and Baek 2015; Aziz et al. 2015, 2016; Patra et al. 2016; Rożalska et al. 2016; Sharma et al. 2016) antioxidant efficacy (Kokila et al. 2015; Patra and Baek 2015; Patra et al. 2016), proteasome inhibitory (Patra and Baek 2015), anticancer (Saratale et al. 2017), anti-

candidal (Patra et al. 2016), larvicidal and pupicidal (Velu et al. 2015; Murugan et al. 2017), growth promoter (Sonkar et al. 2012; Park et al. 2014), DNA detection (Godavarthi et al. 2017), imaging and targeted delivery (Chamundeeswari et al. 2013a, b; Park et al. 2014), pharmaceutical and biomedical practice (Shankar et al. 2014) were also demonstrated by various researchers. Other applications of WMNPs include high power super capacitors (Sun et al. 2013) and cosmetic formulations (Rodrigues et al. 2016).

11.7 Conclusion

Waste management through conventional method is valuable but suffers from tremendous setback. A neoteric technology named “nanotechnology” has expanded its aura to most probably engulf the waste-related concern in near future. This chapter gives a rundown of the general waste management protocol with their related troubles, nanotechnology role in various stages of waste management, nanoconversions from various waste sources, and their budding applications. Despite of being fortunate technology in waste recycling, the uppermost entanglement is the scale up of waste conversion to nanomaterials, as maximum outcome is still executed at laboratory scale. Nanotechnology with the promise to shoot up with its heights in controlling waste in coming future will definitely be effectuated.

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Chapter 12

Synthesis of Nanomaterials Involving Microemulsion and Micellar Medium



Santosh Kumar, Mohammad Y. Wani, and Joonseok Koh

12.1 Introduction

Nanotechnology brings in new techniques to control single atoms and molecules. Nanotechnology comes out from the diverse scientific fields like physics, chemistry, biology, materials, and engineering sciences. Nanomaterials in nanotechnology are defined as small objects that behave as a whole unit in terms of its transport properties and potential application. To control the size and shape of nanoparticles, colloidal self-assembly as confined reaction media offers good advantages. Nanomaterials have been proving attractive due to their important catalytic, electrical, optical, and drug delivery properties accompanied with improved physical properties like mechanical, thermal stability, or chemical passivity. Microemulsion medium is one of the important synthetic methods which control the particle properties like size, geometry, morphology, and surface area (Hu et al. 2009; Pileni 2003; Richard et al. 2017). Many reviews about different aspects of microemulsions have already been written (Malik et al. 2012; Pileni 2008; Lopez-Quintela et al. 2004; Cushing et al. 2004; Shervani et al. 2006). Our intention is to summarize the most recent work carried out in this area, using microemulsion and other micellar methods to control the particle size and morphology of nanoparticles for the synthesis of organic and inorganic nanomaterials.

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12.2 Microemulsions

The word microemulsion was given by Schulman and co-workers in 1959 and mostly he used four component systems like hydrocarbons, ionic surfactants, co-surfactants, and an aqueous phase in his work. The basic observation made by Schulman and co-workers (Schulman et al. 1959) during the titration of a co-surfactant into a coarse microemulsion composed of a mixture of water/surfactant in a sufficient quantity was that a low viscosity, transparent, isotropic, and very stable micro droplet system was formed. These spherical micro droplets had a diameter between 600 and 8000 nm. Since that day microemulsions have found a wide range of applications in pharmaceuticals, cosmetics, detergency, lubrication, and oil recovery.

Microemulsions are multicomponent isotropic, homogeneous, optically transparent and thermodynamically stable dispersion of two immiscible liquids [polar phase (water), a nonpolar phase (oil)] in the presence of an emulsifier or surfactant. On a microscopic level, the surfactant molecules are arranged in different forms to give microstructures in which droplets of oil are dispersed in a continuous water phase (O/W microemulsion) over a bicontinuous “sponge” phase and water droplets dispersed in a continuous oil phase (W/O microemulsion). Microemulsion droplet size is generally 100 times smaller than in traditional emulsions and varies from 1 to 100 nm and therefore the microemulsion system behaves as a nanoreactor for the synthesis of nanoparticles with a low polydispersity. The resulting nanomaterials can be characterized by different techniques like: microstructure optical methods, electron microscopy (SEM, TEM), small-angle X-ray and neutron scattering, rheological measurements, electron paramagnetic resonance (EPR), infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), ellipsometry, and electrical conductivity (Destree et al. 2008; Zhong et al. 2007). Microemulsions have different types, such as water-in-oil (W/O), oil-in-water (O/W), and water-in-CO₂ (W/C).

12.3 Micelles

Micelles are liquid dispersions containing surfactant aggregates in micellar dispersions, the aggregates are made of surfactant only and are usually dispersed in water. Spheroidal aggregates can be formed when surfactant molecules are dissolved in organic solvents that are called as reverse micelles (Pileni 1989). It can be formed in the presence or absence of water where large surfactant aggregates are formed in the presence of water and very small aggregates in the absence of water. Water instantly solubilizes in the polar core to form “water pool” contents, which are characterized by water-surfactant molar ratio. The aggregates having a small amount of water ratio ($W^\circ < 15$) are usually called reverse micelles, whereas the aggregates corresponding to droplets with large amount of water molecules ($W^\circ > 15$) are called microemulsions (Luisi et al. 1986). The micro droplets can be formed in

diverse ways in which the oil-swollen micelles are dispersed in water as oil-in-water (O/W) microemulsion or water swollen micelles dispersed in oil as for water-in-oil (W/O) microemulsion, also known as reverse microemulsion (Fig. 12.1). The formation of these microemulsions depends on the proportion of various components in the system and also on the hydrophilic-lipophilic balance of the surfactant used.

Reverse micelles also known as “Water-in-oil microemulsion are the microemulsion systems in which polar head groups of surfactant molecules are attracted by aqueous core and directed towards inside and hydrocarbon chain i.e. a polar part is attracted by non-aqueous phase and directed towards outside.” By varying the water content, the size and shape of the aqueous core can be easily controlled and uniform size nanoreactors (5–10 nm) can be obtained at a particular ratio of the aqueous phase to the surfactant (Luisiet al. 1986), and it is possible to precipitate the inorganic and organic materials in such nanoreactors (Malik et al. 2012).

12.4 Water-in-Oil (W/O) Microemulsions

Dispersion of water in a hydrocarbon-based continuous phase results in the formation of a “water-in-oil” microemulsion that is mostly situated at the oil apex of a water/oil/surfactant triangular phase diagram. Thermodynamically driven surfactant self-assembly produces aggregates known as reverse micelles (Ekwall et al. 1970); spherical reverse micelles are the most common form which minimizes the surface energy. The polar or ionic components get sequestered into the central cores of these reversed micelles and thereby resulting in the fine dispersion of inorganic and organic materials in oil (Fig. 12.2). It is important to notice that these systems are dynamic in nature, i.e., they frequently collide via random Brownian motion and unite to form dimers, which may swap the contents and then break apart again. Clearly, any encapsulated inorganic reagents will get mixed inside the micelles.

This process is fundamental to nanoparticle synthesis inside reversed micellar “templates,” allowing different reactants solubilized in separate micellar solutions to react upon mixing. Micelles in these systems can be depicted as “nanoreactors” providing a proper environment for the controlled nucleation and growth. In

Fig. 12.1 Typical structure of reverse micelle

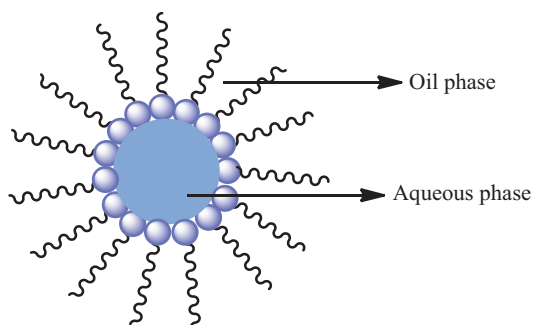
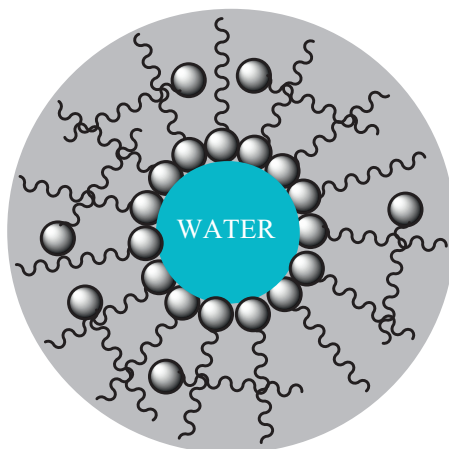


Fig. 12.2 Water-in-oil (W/O) microemulsion



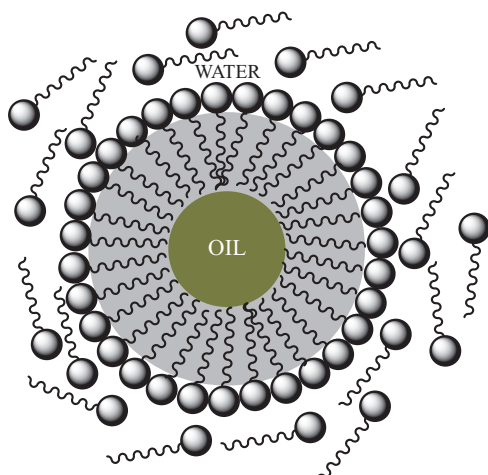
addition, at the latter stages of growth, steric stabilization provided by the surfactant layer prevents the nanoparticles from aggregating (Solanki and Murthy 2011; Lopez-Quintela et al. 2004). Generally, two methods are involved in the synthesis of nanoparticles by using microemulsion techniques. The first method is called the one microemulsion method. This method includes “energy triggering” and the “one microemulsion plus reactant” method. In the energy triggering method, the reaction is initiated by implementing a triggering agent into the single microemulsion which contains a reactant precursor. This fluid system is activated to initiate the reactions that finally lead to the particle formation. For example, to trigger the preparation of nano size gold techniques like pulse radiolysis and laser photolysis have been used (Kurihara et al. 1983). However, in one microemulsion plus reactant method the initiation of the reaction involves the direct addition of a pure reactant (liquid or gaseous phase) into the microemulsion of another reactant. The ions, e.g., metals, are initially dissolved in the aqueous phase of a W/O microemulsion and then the aqueous solution of precipitating agents, e.g., salt NaOH or a gas phase, e.g., NH_3 (g) and CaCO_3 (g), are added to the microemulsion solution. Microemulsion method has been widely used to synthesize various nanoscale crystallines in the last several decades since it is a powerful approach to control the particle size and particle distribution. The synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite was reported by Wang et al. (2014) by using oleic acid as carbon precursor and particle size controller in the microemulsion method.

12.5 Oil-in-Water (O/W) Microemulsions

Microemulsions can normally be prepared in a narrow temperature range (10–20 °C), but this could be overcome by using a mixture of ionic and non-ionic surfactants, which are effective in a wide range of temperatures and exhibit great

solubilizing capacity (Sanchez-Dominguez et al. 2012). By using a suitable mixture of ionic and non-ionic surfactants one could increase the temperature range for producing O/W microemulsions. By increasing the pH of the microemulsion more carboxylic acid groups are neutralized, and the negative charge at the interface provides the double layer which boosts the formation of O/W microemulsion. The driving force for producing O/W microemulsion is the presence of the charged head group. The hydrocarbon core of the normal micelles solubilizes more oil, thus forming swollen micelles which are oil-in-water (O/W) microemulsions. The size of droplets can be tuned in the range of 1–100 nm by using varied concentration of the dispersed phase and surfactant. The use of an aqueous continuous phase lets the incorporation of organic droplets (micelles) and thereby declining the use and human exposure to the organic solvents. Moreover, the micelles (oil-in-water) (Fig. 12.3) can be employed as transporters of a large number of organic compounds or particles, e.g., optical limiting units. The reversed micelles (water-in-oil) can be utilized to carry inorganic compounds. The O/W microemulsions were prepared by following the phase diagram reported by Wang et al. (1995). The exact amounts of surfactant and co-surfactant were dissolved in water, and their compositions were calculated from the phase diagram. Addition of a small volume of heptane on stirring mechanically and then sonicating for 5 min in an ultrasonic bath resulted in the formation of oil-in-water microemulsion. Different microemulsions with various droplet sizes were prepared by varying the concentration of surfactant and dispersed phase. The droplets constituting dispersed phase of an oil-in-water microemulsion can act as transporters of lipophilic solutes across an aqueous environment. Sanchez-Dominguez et al. (2015) have reported formation of TiO₂ and Zn-doped TiO₂ nanoparticles by O/W microemulsion. They used a water/Synperonic91/5/ Isooctane microemulsion system. The microemulsions containing the organometallic precursors (Ti-2EH alone or Ti-2EH and Zn-2 EH) were prepared

Fig. 12.3 Oil-in-water (O/W) microemulsion



by mixing the surfactant, oil component (isooctane plus organometallic precursors), and water. The atomic ratio of the metal precursors was varied from 100:0 to 90:10 of Ti:Zn. The components were mixed by gentle stirring at the appropriate temperature (26 °C), until microemulsions became transparent, fluid, and isotropic. A certain amount of precipitating agent (ammonium hydroxide 25%) was added under vigorous stirring and continued overnight, followed by centrifugation and washing cycles (first with water, then isopropanol, followed by chloroform and finally isopropanol). Finally, it was dried at room temperature for 2 days, ground in an agate pestle and mortar, and calcined at 400 °C (Sanchez-Dominguez et al. 2015).

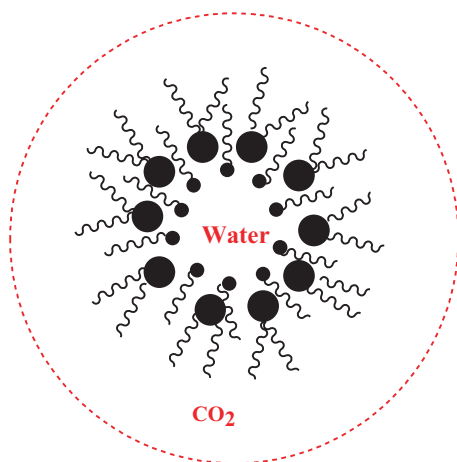
12.6 Bicontinuous Microemulsions

Bicontinuous structure or sponge phase plays a key role in colloidal and interfacial science. It is a complex structure, in which water and oil are used as continuous phases. The sponge exhibits a continuous structure, but it is likely to “fill” the sponge with a liquid. The liquid forms a continuous phase and the material of sponge also form a continuous phase. Bicontinuous structures are more frequently observed in microemulsions, in mesophases, in relatively dilute surfactant solutions, and as structures that cannot be depicted in terms of particles, and in nanophilic systems: zeolites, copolymer molecular metals, volcanic minerals, surfactant-templated synthetic mesoporous oxides (Anderson et al. 2006), and composite media. They are usually not found in discrete micellar aggregates. A bicontinuous arrangement of oil and water channels exists instead of isolated droplets. A comparable amount of water and oil is present in most of the microemulsions and those that are stabilized by lesser amounts of surfactants are of great interest (Kresge et al. 1992). A microemulsion with a mean curvature on the average of zero is a strong indication of bicontinuity. There is no long-range order in the structure of microemulsions and also the mean curvature over the dividing surface is not homogeneous at any given instant. However, we can visualize bicontinuous microemulsion structures using well-defined models (continuous paths between interconnected spheres, distorted lamellae, tubule structures with one of the solvents confined to branched tubes with negligible surface type structures similar to that established for bicontinuous cubic phase) but portray them as being thermally disrupted or melted. The thermodynamic model for bicontinuous microemulsions was first provided by Schulreich et al. (2013) reported bicontinuous microemulsions with extremely high temperature stability based on skin friendly oil, sugar surfactant, and co-surfactant benzyl alcohol. Steudle et al. (2015) demonstrated biocatalysis in bicontinuous microemulsions. The activity of the squalene-hopene cyclase from *Alicyclobacillus acidocaldarius* (AacSHC) towards its natural substrate squalene in bicontinuous microemulsions.

12.7 Water-in-CO₂ (W/C) Microemulsions

Water-in-CO₂ microemulsions have received great attention for the synthesis of nanoparticles (Lim et al. 2002). Carbon dioxide is a smart organic solvent as it is nontoxic, nonflammable, highly volatile, cheap, and environmentally benign in nature. A typical water-in-CO₂ microemulsion system is shown in Fig. 12.4. Water-in-CO₂ (W/C) microemulsions are formed with especially designed surfactants containing “CO₂-philic” fluorocarbon moieties (Mohamed et al. 2016). TiO₂-nanoparticles can be formed by the controlled hydrolysis of titanium tetraisopropoxide (TTIP) in water-in-CO₂ (W/C) microemulsions and stabilized with the surfactants ammonium carboxylate perfluoropolyether and poly(dimethyl amino ethyl methacrylate-block-1H,1H,2H,2H-perfluorooctyl methacrylate) (Lim et al. 2002). The effects of a homologous series of sodium *p-n*-alkylbenzoate hydrotropes in water-in-CO₂ (W/C) microemulsions have been investigated, by comparing the phase behavior and droplet structures (Yan et al. 2015). The W/C microemulsions appeared to be generally stable upon addition of hydrotropes, however, on increasing the alkyl chain length of the hydrocarbon and fluorocarbon moieties of the surfactants, different effects on stability were observed. Yan et al. (2015) research findings were relevant to the understanding of self-assembly of co-adsorbed species in supercritical CO₂, as the hydrotrope layers potentially have significant effects on surfactant packing, and can modify the physico-chemical properties of scCO₂ through formation of worm-like micellar assemblies.

Fig. 12.4 Water-in-CO₂ microemulsions



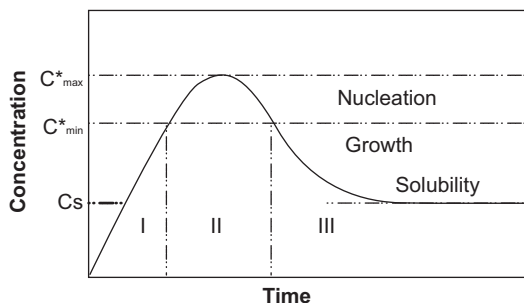
12.8 Mechanism of Nanoparticle Synthesis

In a microemulsion, the aqueous droplets continuously collide and break apart, resulting in a continuous exchange of solution contents. The process of the formation of nanoparticles has been described through the La Mer burst nucleation and Ostwald ripening to describe the change in the particle size. The variation in the size of particles with precursor concentration and with the size of the aqueous droplets in the microemulsion could be explained based on two models. The first is based on La Mer diagram (La Mer and Dinegam 1950), which has been anticipated to explain the precipitation in an aqueous medium and thus is not explicit to the microemulsions. This diagram (Fig. 12.5) is established on the principle that nucleation is a limiting step in the precipitation reaction and demonstrates the variation of the concentration with time during a precipitation reaction. In the first step, there is a continuous increase in concentration with time and once the concentration approaches critical supersaturation value, nucleation occurs, leading to a decrease of the concentration. The nucleation occurs within the concentrations C_{\max}^* and C_{\min}^* and by the growth of the particles by diffusion there occurs a decrease in concentration and the growth of particles continues till the concentration reaches the solubility value. This model has been applied to the microemulsion medium, i.e., firstly nucleation occurs and later only growth of particles occurs. Following this model, the size of the particles will increase continuously with concentration of the precursor or a minimum in the variation of the size with the concentration might be expected. This is because the number of nuclei is constant, and the increase of concentration favors increase in size of particles.

The second model is based on the thermodynamic stabilization of the particles by the surfactant (La Mer and Dinegam 1950) and the nucleation occurs continuously during nanoparticle formation.

The size of the particles remains constant as the precursor concentration and size of aqueous droplets varies. Both the models are limiting models: as the La Mer diagram does not take surfactant stabilization into account, and the thermo-

Fig. 12.5 A typical La Mer diagram



dynamic stabilization model does not take into account that the nucleation of particles are more difficult than the growth by diffusion. Because of the stochastic nature of nanoparticle formation, Monte Carlo simulations can better explain the mechanism of formation of microemulsions. But it is computationally exhaustive due to very large number of micelles considered in a simulation. A mean field approximation with Monte Carlo simulation is possibly required to account for all the probable combinations of various species in the micelles and outcomes of the fission fusion events. The population balance equations with mean field approximation, restricting the maximum number of molecules in a micelle, can be solved and the particle size distribution can be computed from the fraction of nucleated micelles. The several stages involved in the formation of nanoparticles within the water droplets are as: chemical reaction, the nucleation, and the particle growth. In these microemulsions, two different reactants (A and B) are introduced, e.g., in metal oxalate “A” should be a metal ion and “B” should be the oxalate ion. These two microemulsions are continuously stirred and the droplets collide resulting in the interchange of reactants. During this process, the reaction takes place inside the nanoreactor.

12.9 Synthesis of Various Nanomaterials

12.9.1 *Metals*

Metals display important catalytic properties and synthesis of metal nanoparticles is therefore very interesting. Different metal nanoparticles, including silver and gold nanoparticles have been prepared using inverse microemulsion (Barnickel and Wokaum 1990). Rivera-Rangel et al. (2017) have demonstrated a green synthesis of silver nanoparticles using microemulsion with castor oil as the oily phase, Brij 96V and 1,2-hexanediol as the surfactant and co-surfactant, respectively. Geranium (*P. hortorum*) leaf aqueous extract was employed as a reducing agent. The content and concentration of a metallic precursor and geranium leaf extract in the systems used makes it possible to obtain varied sizes of silver nanoparticles from 25 to 150 nm. The O/W synthesis method is more eco-friendly because the continuous phase is water. The most common method involved in the preparation of metal nanoparticles through microemulsions is the reduction method. Nanoparticles of platinum, palladium, rhodium, and Iridium have been prepared by reverse micelles (Boutonnet et al. 1982).

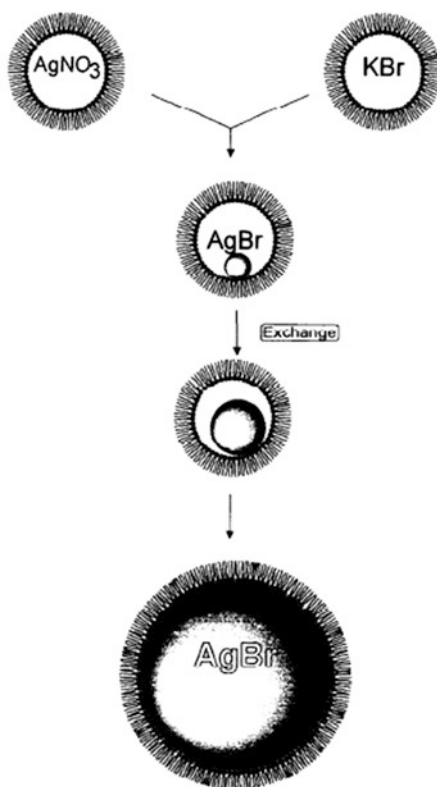
12.9.2 Synthesis of Nanoparticles of Metal Salts

Nanoparticles of silver bromide have been synthesized by mixing of two microemulsions containing the precursor salts AgNO_3 and KBr . The microemulsions are composed of AOT, *n*-heptane, and water. As shown in Fig. 12.6, the role of reaction cage is played by the inner water cores. The initial monomeric AgBr entity is stabilized by AOT adsorption and grows with the fast exchange between water cores (Monnoyer et al. 1995).

12.9.3 Synthesis of Metal Sulfide Nanoparticles

The preparation method is usually applied in the in situ preparation of metal sulfide particles (Chen et al. 2008). Mesoporous CdS nanoparticles have been synthesized using an O/W microemulsion by dissolving the precursor and the precipitating

Fig. 12.6 Model illustrating the role of reaction cage played by the inner water cores (adapted with permission from Elsevier Monnoyer et al. 1995)



agent (CdCl_2 and thioacetamide) in continuous aqueous phase with precipitation of nanoparticles by gamma ray irradiation (Chen et al. 2008). The average diameter of the particles was found to depend on the relative amount of Cd^{2+} and S^{2-} .

12.9.4 Metal Oxides Nanoparticles

CeO_2 , ZrO_2 , $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, and TiO_2 nanoparticles are synthesized by using oil-in-water microemulsions in contrast to the typically used water-in-oil microemulsion method (Sanchez-Dominguez et al. 2010; Boutonnet and Sanchez-Dominguez 2017). The specific surface area of the nanomaterials was 200–370 $\text{m}^2 \text{g}^{-1}$ and the particle size was very small ($\sim 2\text{--}3 \text{ nm}$). CeO_2 , ZrO_2 , $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, and TiO_2 nanoparticles can be prepared by water/Synperonic[®]10/6/hexane O/W microemulsions. The microemulsion containing an organometallic precursor has been prepared by mixing suitable amounts of the surfactant, the oil component, and deionized water with composition as: 64.5% water, 21.5% surfactant, and 14% oil phase for TiO_2 , ZrO_2 , and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, and 60% water, 20% surfactant, and 20% oil phase for CeO_2 . To obtain a transparent, homogeneous, and fluid isotropic phase, the mixture was magnetically stirred at 25 °C (for TiO_2) or 35 °C (for CeO_2 , ZrO_2 , and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$) and then the microemulsion was kept at 35 °C. A turbid yellow color for CeO_2 and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ nanoparticles and turbid white for ZrO_2 and TiO_2 nanoparticles appeared on adding 25 wt% NH_3 , till pH 10–11 was achieved. The reaction mixture was stirred overnight, followed by centrifugation and washed several times with ethanol and chloroform and finally dried at 70 °C. Calcination was done at a heating rate of 5 °C min^{-1} and keeping at 400 °C during 2 h in an air atmosphere (Sanchez-Dominguez et al. 2010).

12.9.5 Synthesis of Magnetic Nanoparticles

Iron oxide nanoparticles are of great interest because of their unique magnetic properties. The magnetic nanoparticles were first formed in micelles from the oxidation of Fe^{2+} salts to form Fe_3O_4 and Fe_2O_3 (Inouye et al. 1982). This reaction was carried out in a sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/isooctane system to form spherical nanoparticles with surprisingly tight size distributions of less than 10%. Okoli et al. (2012) demonstrated the synthesis of magnetic iron oxide nanoparticles for protein binding and separation, obtained from W/O and O/W microemulsions with sizes ranging from 2 to 10 nm. For synthesis via O/W microemulsion reaction method, the microemulsion consisted of a non-ionic surfactant (Synperonic 10/6), oil phase containing the iron precursor (hexane plus iron(III) 2-ethylhexanoate) and aqueous phase. It was prepared by the addition of organometallic precursor solution to the three components and stirring at 30 °C until a homogeneous, transparent brownish isotropic phase was obtained. The precipitating agent (NH_3) was added to

the stirring mixture till pH 11 was achieved to precipitate the magnetic iron oxide nanoparticles. The reaction mixture was kept stirring at 30 °C for 48 h. The magnetic nanoparticles were obtained by centrifugation and later washed and dried. For synthesis via the W/O microemulsion method, it consisted of a cationic surfactant (CTAB), co-surfactant (1-butanol), oil phase (*n*-octane), and aqueous phase. The aqueous phase contained the Fe salt precursors in a mole ratio of 2:1 [FeCl₃/FeCl₂]. The addition of the precursor solution to the mixture of CTAB/1-butanol/*n*-octane gave a way for the formation of a microemulsion. A magnetic nanoparticle was achieved by adding the precipitating agent (NH₃) to the microemulsion containing the precursor upon vigorous stirring until pH 11 was achieved. The obtained magnetic nanoparticles were separated by centrifugation, washed, and dried at 70 °C (Okoli et al. 2012). Recently, Hu et al. (2017) developed a novel method to synthesize iron oxide nanoparticles in situ in O/W microemulsions for improving oil recovery. Iron oxide nanoparticles were in situ synthesized in microemulsions containing brine, *n*-hexane, mixture of SDS and Span 80 as the surfactants, and propyl alcohol as the co-solvent.

12.9.6 Synthesis of Mn-Zn Ferrite Nanoparticles

Pemartin et al. (2014) have synthesized Mn-Zn ferrite magnetic nanoparticles via oil-in-water (O/W) microemulsion reaction method. By variation of the precipitating agent and the oil phase concentration, distinctive characteristics were found. The microemulsions containing organometallic precursors (Fe-2EH, Zn-2EH, Mn-2EH, 2 wt% solution of metal in hexane) were synthesized by mixing the surfactant, oil component, and water. The surfactant: water weight ratio was 25:75 and the concentration of oil component was 12 or 20 wt%; this corresponds to a water:surfactant:oil weight ratio of 66:22:12 and 60:20:20, respectively. The atomic ratio of the metal precursors was 2:0.5:0.5 of Fe:Mn:Zn. The components were mixed by stirring gently at appropriate temperature (25 °C for sample with 12 wt% oil and 40 °C for sample with 20 wt% oil), until microemulsions became brown transparent, fluid and isotropic. Then, a certain amount of precipitating agent (aqueous solution of 0.5 M TMAH or 2.5 M NaOH) was added under vigorous stirring up to pH = 12.5. Due to the high toxicity of TMAH, and its large tendency to adsorb onto the surface of iron oxides, a lower concentration to reach the same final pH was used to facilitate its removal from the system as the obtained nanoparticles find potential application in biomedicine. The reaction mixture was stirred overnight, followed by centrifugation and repeated washings with a mixture of water/ethanol and dried in the oven at 70 °C for 2 days. Aubery et al. (2013) have reported microemulsions as reaction media for synthesizing mixed oxide nanoparticles and the relationships between microemulsion structure, reactivity, and nanoparticle characteristics. To determine the effect on the formation of Mn-Zn ferrite nanoparticle, phase behavior, dynamics,

and structure of W/O microemulsions of the aqueous solution/Synperonic13-6.5/1-hexanol/isooctane system were studied. The co-surfactant 1-hexanol caused a decrease in the microemulsion regions in comparison to the systems without co-surfactant; however, overlap of microemulsion regions with precursor salts (PS) and precipitating agent (PA) was attained at lower S/O ratios in the systems, compared to the system without co-surfactant. PA microemulsions at 50 °C are non-percolated while the PS microemulsions are percolated.

12.9.7 Nanowires

The nanomaterials fabricated in the reverse micelles are spherical particles in most cases. However, the variations in the properties of nanoparticles are affected by the shape of nanoparticles. For example, cubic Pt nanoparticles have been synthesized and showed extremely good catalysis, selectivity, and activity (Ahmad et al. 1996). Platinum nanowire with high surface area ($32.4 \pm 3.6 \text{ m}^2 \text{ g}^{-1}$) and average diameter (2.2 nm) has been synthesized by the reduction of a platinum complex by NaBH_4 in the presence of cetyltrimethylammonium bromide in a two-phase water-chloroform system (Song et al. 2007). Qi et al. (1997) synthesized cubic BaSO_4 nanoparticles by using reverse micelles of TX-100/hexanol-cyclohexane/water. They confirmed that the water content significantly affected the shape of the nanoparticles in the reverse micelles. In contrast, in the non-ionic reverse micelle 0.1 M BaCl_2 and Na_2CO_3 aqueous solution was added to 0.2 MC_{12}E_4 /cyclohexane solution, and mixing the two reverse micelles, BaCO_3 nanowires were obtained.

12.9.8 Nanorods

The reverse micellar route was adopted for the preparation of zinc oxalate nanorods for which the microemulsion was prepared with CTAB acts as a surfactant, 1-butanol as co-surfactant, isooctane as nonpolar phase, and 0.1 M aqueous solution of Zn^{2+} and $\text{C}_2\text{O}_4^{2-}$. Microemulsion I contained 0.1 M zinc nitrate solution while microemulsion II contained 0.1 M ammonium oxalate solution, both were mixed slowly and stirred overnight on a magnetic stirrer. The weight fraction of the components in the microemulsion was 16.76% of CTAB, 13.9% of *n*-butanol, 59.29% of isooctane, and 10.05% of aqueous phase. The precursor was separated from the surfactant and nonpolar phase by centrifugation at an interval of every 2 h of reaction. The precursor was then washed with a mixture of 1:1 chloroform/methanol to remove the surfactant and then dried at room temperature. These zinc oxalate nanorods synthesized at different time intervals were then calcined at 300 °C for 6 h to obtain the resulting zinc oxide (ZnO) nanostructures (Sharma and Ganguli 2014).

12.9.9 Nanocomposites

Reverse micelle is an important method for synthesizing the composite nanoparticles. Composite nanoparticles like CdS-ZnS and CdS-Ag₂S have been successfully synthesized by reverse micelles (Han et al. 1998). For core shell nanoparticles synthesis, two steps are involved; in first step, the core nanoparticles are formed in the reverse micelles and the second step involves the growth of shell particle on the core. CdS/ZnS is a typical example of shell-core type composite nanoparticles (where CdS is the core and the ZnS is the shell) synthesized by mixing the reverse micelles containing Cd²⁺ and S²⁻ in a 1:2 ratio resulting in the formation of a core CdS reverse micelle solution. In this reverse micelle S²⁻ is in excess. After several minutes, Zn²⁺ containing reverse micelle is added, which results in the precipitation of ZnS inside the core of CdS nanoparticles and a shell-core type CdS/ZnS composite nanoparticle is obtained. Using this method, CdS/ZnS and ZnS/CdS composite nanoparticles have been synthesized. Another type of composite nanoparticle has been reported to contain two metals but not in the 1:1 ratio. Chen and Chen (2002) have reported the synthesis of Au-Ag bimetallic nanoparticles in water/AOT/isooctane microemulsions (Chen and Chen 2002). Wang et al. (2014) have synthesized ultrafine Li₄Ti₅O₁₂/C composite by microemulsion with oleic acid as carbon precursor and particle size controller. Recently, Pal et al. (2017) have demonstrated fiber formation in emulsion electrospinning by revealing the viscoelastic interaction between dispersed and continuous phase. Composite electrospun matrices of poly(ϵ -caprolactone) with or without hydroxyapatite were developed from an oil-in-water emulsion. The fiber formation and uniformity were clearly governed by the viscoelastic interaction between the continuous and dispersed phase. Caging of droplets by optimal quantity of poly(vinyl alcohol) (PVA) in continuous phase resulted in uniform stretching and coalescence of droplets (Pal et al. 2017).

12.10 Synthesis of Medium-Chain-Length poly-3-Hydroxyalkanoates (mcl-PHA) Nanoparticle

Ishak and Annuar (2017) demonstrated the effect of temperature on the phase behavior of medium-chain-length poly-3-hydroxyalkanoates nanoparticle. The O/W emulsion was used as template to produce mcl-PHA-incorporated nanoparticle. Water-to-organic phase, oil-to-surfactants, and cremophor EL-to-Span 80 ratio were optimized using response surface methodology with the size of oil droplets produced (20–30 nm).

12.11 Synthesis of Organic Nanomaterials

Synthesis of organic nanoparticles is usually done oil-in-water microemulsions, also known as microemulsion polymerization (Vaucher et al. 2002). However, this technique didn't make much progress due to the phase separation occurring during the process. Margulis-Goshen and Magdassi (2012) have reviewed the methods used to produce organic nanomaterials from microemulsions. Atik and Thomas (1981) reported the use of microemulsion polymerization for the preparation of organic nanoparticles, using a CTAB/styrene/hexanal/water O/W microemulsion system. They obtained monodisperse latex nanoparticles of diameters 35 and 20 nm. The reaction was carried out either thermally using azobisisobutyronitrile (AIBN) or radiolytically. The particles formed were transparent up to 60% of water in the microemulsion systems. Several other organic nanoparticles of cholesterol, retinol rhodiarome, and rhovanil have been synthesized using different microemulsion systems such as AOT/heptane/water, triton/decanol/water, and CTABr/hexanol/water microemulsions (Destree and Nagy 2006). Generally, the active organic compounds are directly precipitated in the aqueous cores of the microemulsion and are detected and observed with iodine vapor and transmission electron microscope. The mechanism of the formation of nanoparticles consists of several steps. The solution of the active compound in an appropriate solvent penetrates inside the aqueous cores by crossing the interfacial film. The solvent plays a key role in carrying the active compound into the aqueous cores, where it gets precipitated due to its insolubility in water and thereby resulting in the formation of nuclei. The growth of nuclei can occur due to the exchange of an active compound between the aqueous cores, and finally these nanoparticles are stabilized by the surfactants (Nagy and Mittal 1999). Lavaud et al. (2017) have developed a simple procedure to prepare a new Prussian blue (PB)-lecithin reverse micellar system comprising PB nanoparticles within the Aonys formulation containing peceol, β -sitosterol, lecithin, ethanol, and water. The lecithin-containing reverse micellar systems including ultra-small PB nanoparticles which are stable over time, while lecithin-free reverse micellar systems show aggregation of the nanoparticles, even for freshly mixed solutions, leading to system destabilization and PB precipitation with time. Using PB nanoparticles within a reverse microemulsion for in vivo Cs⁺ (caesium) elimination has great advantages (Lavaud et al. 2017).

12.12 Conclusion

Nanotechnology today is considered to be a mature interdisciplinary scientific field, where the applications are enormous. However, the growing demand of new advanced nano-technologies necessitates the development of new methods

to synthesize nanoparticles of desired size, morphology, and properties. To this end, various methods have been successfully developed and used to fine tune the particle size and morphology of the nanoparticles. Microemulsion method is developed long time back, holds promise even today because it allows controlling the particle size and morphology, offers thermodynamic stability, monodispersity, homogeneity, and easy synthetic procedure. The particle size and morphology can be controlled by judicious choice of the various components of the microemulsion and other micellar media. However, the use of microemulsion method in pharmaceutical industry has some concerns like the toxicity of the surfactant and stability of the microemulsion which depends on temperature and pH, and these parameters change when the microemulsion is delivered inside the body. If these concerns are addressed, this method would be greatly helpful in the pharmaceutical industry and drug delivery field.

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Chapter 13

Hydrothermal Nanotechnology: Putting the Last First



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13.1 Nanotechnology: An Introduction

Nanoparticles: Last in the line above the atom, the most difficult to find, and the hardest to learn from. Like atoms nanoparticles are present around us everywhere and are produced by variety of sources like vacuum cleaners, laser printers, candle flames and many more. But unlike atoms we can see the structure of nanoparticles and the breakthrough came with the advent of electron microscope in 1931, when German scientists Ernst Ruska and Max Knoll built the first Transmission Electron Microscope, or TEM. Scientists could now explore the structure of organic molecules that make up the human body, such as proteins, and inorganic materials, such as metals, by examining a cross section of a sample (Boysen and Boysen 2011).

As the matter at the nanoscale behave differently than bulk matter (Rao et al. 2006), nanotechnology has evolved as a recognized branch of science and has broad reach across several scientific disciplines and many industries. Some consider that the general concept of nanotechnology started with a talk that Richard P. Feynman gave in 1959 at the California Institute of Technology. In his talk titled “There is plenty of room at the bottom” the American theoretical physicist asked the question “what would happen if we could arrange the atoms one by one the way we want them?” opened up the possibilities of the nanoscale world, controlling the atoms and molecules that make up matter.

In spite of the fact that the nanotechnology has been around us since 50 years, there is no unanimity about its definition. The word nano comes from the Greek

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word “*nanos*”, meaning dwarf and is used as a scientific prefix that stands for 10^{-9} or 1 billionth; the most commonly accepted definition is probably “*Nanotechnology is the study and use of structures between 1 nanometer (nm) to 100 nanometer (nm) in size*”. The European Commission offers the following definition “*Nanotechnology is the study of the phenomena and fine tuning of materials at atomic, molecular and macromolecular scale, where properties differ significantly from those at the larger scale*” (Boysen and Boysen 2011). The National Nanotechnology Initiative offers the following definition “Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale”. These two are among the many definitions available from different scientific and non-scientific communities like Foresight institute, National Nanotechnology Initiative, IBM Watson Research Center and is based on the fact that materials at the nanoscale have novel properties.

13.2 Synthesis of Nanomaterials

Nanoparticle synthesis refers to methods for creating nanoparticles. The synthesis of nanoparticles with a purpose of having better control over particles size distribution, morphology, purity, quantity and quality by employing environment-friendly economical processes has always been a challenge for the researchers.

Two historical evidences—medieval stained glasses and the Lycurgus cup—indicate that humans have been making and using nanoparticles for nearly 2000 years (Kuno 2012). The Roman Lycurgus cup, a relic from the fourth century AD is a well-preserved example of production of metal nanoparticles. What make the cup special are its unique colours that change depending on viewing angle. The light directly transmitted through the cup appears red whereas that transmitted at an angle appears green. This multicolour phenomenon stems from the presence of metal nanoparticles embedded within it as studied by Barber and Freestone (1990) through TEM. Their study on a small fragment of the cup revealed the presence of 50–100 nm diameter gold/silver nanoparticles. The other interesting observation is by Fredrickx et al. (2002) who confirmed the presence of gold nanoparticles in a red glass fragment found in the excavated workshop of Johann Kunckle, a well-known seventeenth century glass maker. The modern era of scientific probing to nanoparticles begins with Faraday’s work (1857) on gold nanoparticles.

Nanoparticles synthesis has taken a giant leap since Faraday’s time when colloidal metal nanoparticles and semiconductor quantum dots were first time made to the formation of buckyball by vapourizing graphite using a laser in an atmosphere of helium gas by Kroto et al. (1985). The buckyball is also known as fullerene or C₆₀ for the 60 carbon atoms it contains. It is spherical in shape having interlocking hexagons and pentagons of carbon atoms, similar to those in a soccer ball. After the discovery of buckyballs, came the discovery of tiny needles of carbon that run

anywhere from 1 to 100 nm in diameter, by Sumio Iijima, who named them carbon nanotubes (Iijima and Ichihashi 1993). These tubes are made of carbon atoms connected in hexagons and pentagons like buckyballs but in a cylindrical shape. Figure 13.1 shows a representative diagram of a graphene sheet, a single wall carbon nanotube and a buckyball.

Nanomaterials come in variety of flavours: Fractals (Mandelbrot 1983; Bunde and Havlin 1996), porous materials (Srivastava et al. 2002), zeolites (Dyer 1988), fullerenes (Kroto et al. 1985), micelles (Yin and Wang 1997; Sun and Murray 1999), self-assembled monolayers (Wang 1998), etc. A broader classification for the different types of nanomaterials can be organic nanoparticles (Dendrimers, micelles, liposomes and ferritin), inorganic nanoparticles (Metal and metal oxide based) and carbon-based nanoparticles (fullerenes, graphene, carbon nano tubes (CNT), carbon nanofibres and carbon black).

There are various nanomaterial synthesis techniques available nowadays (Fig. 13.2), namely mechanochemical, chemical, hydrothermal, flame combustion, emulsion precipitation, etc.; each method varies in effectiveness and has its own advantages and disadvantages. The performances of nanomaterials are closely related to the ways they are synthesized, but they are all based on one of the two *fundamental mechanisms: Energy maximization (Top-down approach) and Supra-Molecular Chemistry (Bottom-up approach)*.

13.2.1 Synthesis of Nanomaterials from Above and Below

Nanoparticles can be derived from larger molecules, or synthesized by “bottom-up” methods. In general, top-down and bottom-up are the two main approaches for nanomaterial synthesis.

- Top-down: size reduction from bulk materials.
- Bottom-up: material synthesis from atomic level.

Top-down approach aims at pushing hard and reaching down. It begins with a pattern generated on a larger scale, then reduced to nanoscale by breaking up larger

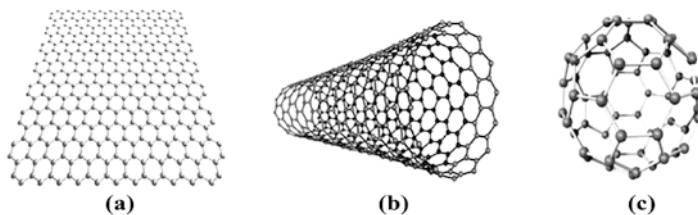


Fig. 13.1 Representative diagrams of (a) a graphene sheet, (b) a carbon nanotube and (c) a buckyball

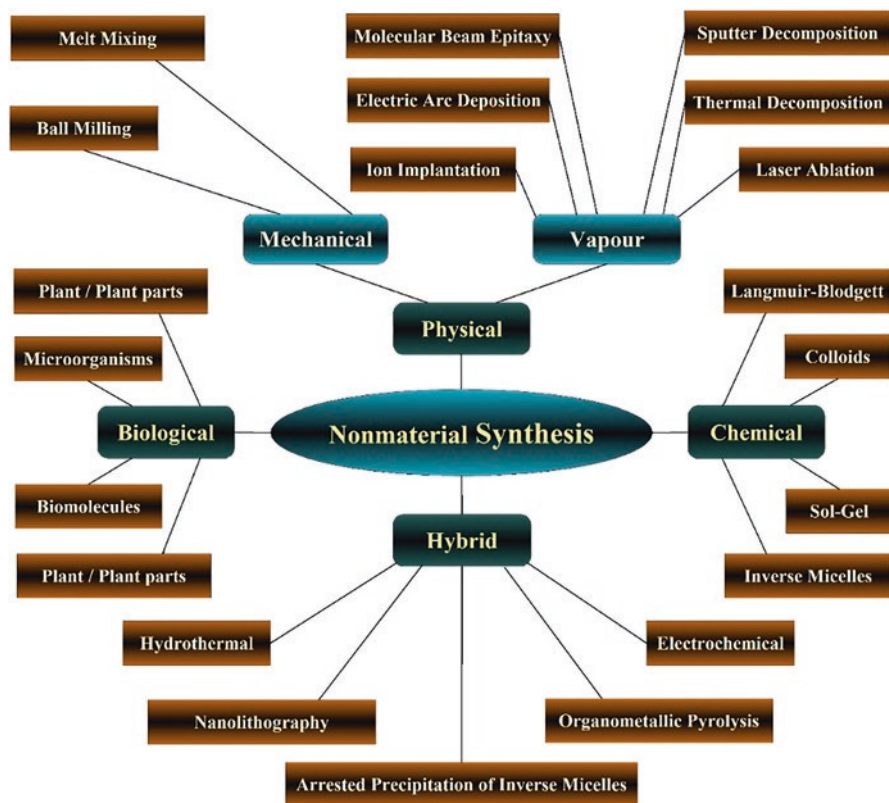


Fig. 13.2 Nanomaterial synthesis techniques

particles using physical processes like crushing, milling, grinding, etc. This method is currently used to manufacture computer chips as well as other products we use every day; however, the biggest problem with the top-down approach is the imperfection of the surface structure. Such imperfection would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials. Usually this route is not suitable for preparing uniformly shaped materials, and it is very difficult to realize very small particles even with high energy consumption. Also this method is neither cheap nor quick to manufacture and thus not suitable for large-scale production.

Bottom-up approach refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster. This route is more suitable for preparing nanoscale materials of uniform size, shape and distribution. The bottom-up approach is relatively new approach, in the theoretical stage, with researchers continuously upgrading the experimental techniques to synthesize nanomaterials by this technique. In 1977, Eric Drexler, while still a student at MIT, first outlined the fundamental bottom-up approach to nanotechnology in which he described how we might manipulate individual atoms and thereby synthesize

materials. Drexler who was the first to be granted Ph.D. in Molecular Nanotechnology postulated that we could use tiny machines called molecular assemblers, to build just about anything-using common chemicals (Drexler 1986, 1992; Bimberg et al. 1999). Few high-tech bottom-up techniques for synthesizing quantum wells and quantum dots are: Molecular Beam Epitaxy (MBE), colloidal growth, arrested precipitation, inverse micelles, etc. (Drexler 1986; Bimberg et al. 1999; Turkevich et al. 1951; Brust et al. 1994; Rossetti et al. 1985).

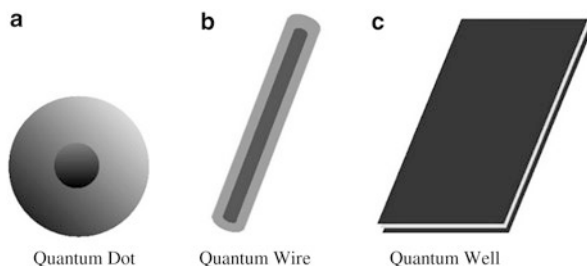
There are three generic types of nanostructures important to us. The classification is based on the dimensions in which a carrier (electrons and holes) is free to move. These structures are alternatively referred to as low dimensional systems and possess a given dimensionality, the schematic illustrations of which are given in Fig. 13.3:

- Quantum dots (zero-dimensional system)
- Quantum wires (one-dimensional system)
- Quantum wells (two-dimensional system)

In a particular low dimensional nanostructure, carrier confinement occurs in a particular direction if the physical thickness of the material in that direction becomes smaller than the characteristics or de-Broglie length of mobile carriers. In a quantum dot, the structure is narrow along all three directions of a co-ordinate system. It is usually depicted by a small spherical particle of radius smaller than the characteristic de-Broglie wavelength of carriers in that material (Bera et al. 2010). In a nanowire, the material is stretched along a single direction with other two orthogonal dimensions much narrower (Schmid 2005). The cross-sectional geometry of a nanowire may have different shapes such as circular, rectangular or square. Finally, in quantum well the carriers have one degree of confinement and two degree of freedom (Zory 1993; Rao et al. 1999).

The controlled synthesis of desirable composition, size, shape and crystal structure is of considerable interest because of its potential application in obtaining materials with wide technological applications. Among the various synthesis techniques mentioned in Fig. 13.2, hydrothermal technique has proven to be an excellent method for the synthesis of different chemical compounds.

Fig. 13.3 Schematic illustration of (a) quantum dot, (b) quantum wire and (c) quantum well



13.3 Hydrothermal Method

The term hydrothermal usually refers to any heterogeneous reaction in the presence of aqueous solvents under elevated pressure and temperature conditions to dissolve and recrystallize materials that are relatively insoluble under ordinary conditions. The word was first coined by British Geologist, Sir Roderick Murchison (1792–1871) in explaining the formation of various rocks and minerals in earth's crust. It all started with developing an understanding of the mineral formation process in nature that is how in the presence of water under elevated pressure and temperature formation of minerals and rocks takes place in earth's crust. The Greek prefix hydro (The Greek word for hydro is $\text{h}\ddot{\upsilon}\delta\omicron\rho$ — $\ddot{\upsilon}\delta\omega\rho$) means water and thermal (The Greek word for thermal is $\text{th}\acute{\epsilon}\rho\mu\tilde{\epsilon}$ — $\theta\acute{\epsilon}\rho\mu\eta$) means heat. In the last three decades hydrothermal technique has become a very popular means to simulate the natural conditions existing under the earth's crust, and synthesizing them in laboratory (Byrappa and Yoshimura 2001), still there is no unanimity about its definition, neither there is any unanimity about the critical values of temperature and pressure above which the process can be categorized as hydrothermal. There have been several definitions of hydrothermal technique since its advent and are listed in Table 13.1.

As mentioned research on hydrothermal technique started in the middle of the nineteenth century by geologists and the initial work related to hydrothermal synthesis of materials is attributed to R.W. Bunsen, who grew barium and strontium carbonate at temperatures above 200 °C and pressures above 100 bars in 1839 (Bunsen 1848). After that in 1845, C.E. Schafhautl observed the formation of small

Table 13.1 Definition of hydrothermal synthesis prescribed by different researchers

Author (year)	Definition
Morey and Niggli (1913)	In the hydrothermal method the components are subjected to the action of water, at temperatures generally near though often considerably above the critical temperature of water (~370 °C) in closed bombs, and therefore, under the corresponding high pressures developed by such solutions
Laudise and Parker (1970)	Hydrothermal growth means growth from aqueous solution at ambient or near-ambient conditions
Lobachev (1973)	Defined it as a group of methods in which crystallization is carried out from superheated aqueous solutions at high pressures
Rabenau (1985)	Defined hydrothermal synthesis as the heterogeneous reactions in aqueous media above 100 °C and 1 bar
Byrappa (1992)	Defines hydrothermal synthesis as any heterogenous reaction in an aqueous media carried out above room temperature and at pressure greater than 1 atm
Roy (1994)	Declares that hydrothermal synthesis involves water as a catalyst and occasionally as a component of solid phases in the synthesis at elevated temperature (>100 °C) and pressure (greater than a few atmospheres)
Yoshimura and Suda (1994)	Proposed the following definition: reactions occurring under the conditions of high-temperature–high-pressure (>100 °C, >1 atm) in aqueous solutions in a closed system

quartz crystals upon transformation of precipitated silicic acid in a steam digester (Schafhautl 1845). Thereafter, Wöhler in 1848 recrystallized apophyllite by heating apophyllite in water solutions at 180–190 °C under 10–12 atm pressure (Wöhler 1848). The next significant contribution was by H. De Senarmont, in the year 1856 where he synthesized six-sided quartz prism with pyramidal termination. Then it was French mineralogist, Daurree (1857), who first used a steel tube to synthesize quartz and wollastonite at about 400 °C with water as a solvent. Barrer in 1940 succeeded in synthesizing for the first time analcime, a member of zeolite group, using the hydrothermal technique (Barrer 1948). This initiated the flurry of artificial production of bulk single crystals of quartz and zeolites during late 1930s and 1940s. In 1950–1970, Roy and co-workers used the hydrothermal process to synthesize systematically for the first time the whole range of 7, 10 and 14 Å clay minerals and selected zeolite families with an enormous range of compositions (Roy and Roy 1955). The hydrothermal technique received a wide acceptance due to its technological efficiency in developing bigger, purer and dislocation-free single crystals and practically all inorganic species, starting from native elements to the most complex oxides, silicates, germanates, phosphates, chalcogenides, and carbonates have been obtained by this method. The year 1990 marks the beginning of the work on the processing of fine to ultra-fine particles with a controlled size and morphology. Nowadays hydrothermal researchers are able to understand the mechanism involved in hydrothermal synthesis owing to the advent of optical instruments which can probe up to the atomic and subatomic structures. Among the different chemical methods, hydrothermal synthesis is often preferred due to its simplicity, allowing the control of grain size, morphology and degree of crystallinity by easy changes in the experimental procedure. Thus hydrothermal technique can control the formation process and yield even sub-micrometre to nanosize crystalline products with desired properties.

Today, hydrothermal technique has found its place in several branches of science and technology, and is of use for people of several streams like material scientists, earth scientists, material engineers, metallurgists, physicists, chemists, biologists and others. A number of other techniques find its origin in the hydrothermal technique; at the core is the hydrothermal technique, and the other techniques have their roots attached to it as depicted in Fig. 13.4.

The other major reason for the success of hydrothermal technique is that it meets the global concern and awareness for the development of environment-friendly materials. In few other techniques such as solid-state reaction method, hazardous volatile gases are emanated during the high temperature sintering. Considering the fatal affects which these hazardous substances cause to living organism and in general to environment, the hydrothermal technique occupies a unique place in modern science and technology. Hydrothermal technique is in line with the development of ecologically benign, “green” compounds with the recent RoHS and WEEE legislation stipulated by the EU (Jha and Prasad 2010).

Fig. 13.4 Hydrothermal processing: an interdisciplinary technique



13.4 Exploring the Role of Solvent

In any hydrothermal system or reaction, the role played by the solvent under the action of temperature and pressure is very important. Water is one of the most important solvents used for the purpose and its properties such as vapour pressure, density, surface tension and viscosity are greatly changed under hydrothermal conditions (Meng et al. 2016). It was most popularly used as a hydrothermal mineralizer in all the earlier experiments due to the advantages that water is cheaper than other solvents, and it can act as a catalyst for the formation of desired materials by tuning the temperature and the pressure. It is nontoxic, nonflammable, noncarcinogenic, nonmutagenic, and thermodynamically stable. Another advantage is that water is very volatile, so it can be easily removed from the product. However, several compounds do not show high solubility for water even at supercritical temperature, and hence the size of the crystals or minerals obtained in all the early hydrothermal experiments did not exceed thousandths or hundredths of a millimetre. Therefore, the search for other suitable mineralizers began. The other reason behind the investigation of different solvents in the chemical reactions is to bring down the pressure and temperature conditions close to ambient conditions and to increase the solubility of the desired compound. A variety of aqueous and non-aqueous solutions were tried to obtain highly crystalline products. Depending upon the type of solvent used in such chemical reactions, a common term in use is solvothermal synthesis. Specifying the solvent, solvothermal synthesis can be classified as: hydrothermal, glycolthermal, ammonothermal, many more.

Glycolthermal process is a special class of solvothermal process in which organic solvent, especially glycols, is used to prevent the formation of hard agglomerations during crystallization. Though the reaction mechanism in non-aqueous solutions is complex, then also combining glycols and hydrothermal treatment is a successful method for preparing highly crystalline nanoparticles with narrow size distribution and low aggregation. Very few investigations have been reported dealing with the

use of glycol to synthesize crystalline ceramic powders under hydrothermal conditions (Kil et al. 2015).

Ammonothermal synthesis uses ammonia instead of water to epitomize the hydrothermal synthesis as ammonia resembles water in its physical properties (Richter and Niewa 2014). Since ammonia is more reactive than water in terms of metal solubility, so less harsh temperature and pressure conditions are required to carry out the process. The first ammonothermal syntheses were carried out in the year 1960 by Juza and Jacobs and subsequently followed by Jacobs and co-workers (Juza and Jacobs 1966; Juza et al. 1966; Jacobs and Schmidt 1982). The chemists working in the supercritical region dealing with the materials synthesis, extraction, degradation, treatment, alteration, phase equilibria study, etc. prefer to use the term supercritical fluid technology (Byrappa and Adschiri 2007).

13.5 Hydrothermal Synthesis

Hydrothermal synthesis or crystal growth under hydrothermal conditions is typically carried out in a pressurized vessel called an autoclave. In an autoclave, nutrient is supplied along with solvent, which may be water or any other chemical. To enhance the process, some amount of surface modifiers is also mixed. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal. The block diagram of hydrothermal synthesis procedure is as shown in Fig. 13.5.

In hydrothermal method, the involved reaction time is long and highly corrosive salt is used to synthesize inorganic materials, so the autoclave must be capable of sustaining highly corrosive reaction system at high temperature and pressure for a longer time duration. Thus the major factors deciding the choice of a suitable autoclave are temperature, pressure and the ability of the autoclave material to resist corrosion in that pressure-temperature range for a given solvent. Other desirable conditions for autoclave are:

- Length should be sufficient enough to set a desired temperature gradient.
- The choice of autoclave material should be such that it is inert to acids/bases and oxidizing agents.
- High creep-rupture strength (is measured by measuring the span of time a material can withstand without breakdown or rupture when subjected to stress at a given temperature).

An autoclave satisfying the above conditions is practically hard to design. Most autoclaves are designed to satisfy the specific need of a given project. Stainless steel, cobalt-based and titanium-based alloys are mostly employed for making autoclave due to their superior corrosion resistance and high creep-rupture strength (Laudise and Nielsen 1961; Clauss 1969). Additional care must be taken to counter the fact that under various corrosion processes the actual strengths of alloys are less

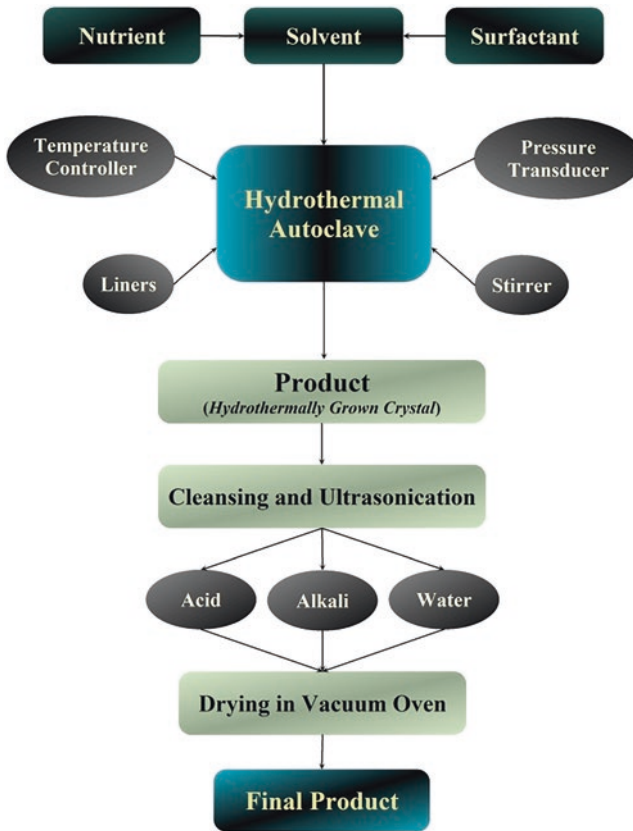


Fig. 13.5 Hydrothermal synthesis procedure

than their strengths under ideal conditions. In addition, it must be noted that the creep-rupture strengths decrease significantly with increasing temperature (Byrappa and Yoshimura 2001), thereby lowering the maximum permissible pressure of an experiment at higher temperature.

The corrosion which the autoclave material encounters at high temperature and pressure during hydrothermal process comes under either of the following three, namely, crevice corrosion, stress corrosion cracking and inter-crystalline corrosion. The crevice or crack can be taken care off by properly polishing the inner surface of the vessel. Inter-crystalline corrosion can be taken care off by using low carbon grade of stainless steels, by high-temperature solution heat treatment and alloying with small amounts of metals (Nb, Ta and Ti) forming very stable carbides. Stress corrosion can be retarded through proper annealing of the alloy used for making autoclaves, and through the use of molybdenum containing austenitic steels.

In addition, systems containing hydrogen cannot be synthesized by hydrothermal technique as hydrogen reacts badly at high temperature with the alloys used for preparing autoclaves and can reduce the strength of autoclaves either by hydrogen

embrittlement, irreversible hydrogen damage, or metal-hydride formation. These problems could be overcome through careful selection of alloys containing small additives such as Ti, Mo and V; heating in H₂-free atmosphere and using alloys with low thermodynamic activity.

Obtaining a contamination-free, high purity crystal is one of the major requirements of any synthesis method. A major setback to this requirement in hydrothermal method is the use of highly corrosive mineralizer that reacts with the material of the autoclave causing a permanent decay. This can be prevented by suitable lining of the inner walls of the autoclave or by placing separate liners over the inner surface. Among very early users of liners are Daurree (1857) and Allen et al. (1912), who either used pure glass or some variants of glass accompanied with steel tube as host for the glass tube, then came the era of steel autoclave and noble metal lining. Different metal linings are used depending upon the solvent medium (Litvin and Tules 1973) (Table 13.2).

13.6 Types of Hydrothermal Method

In hydrothermal method, the physical parameters, which can be controlled externally, are temperature, pressure, time and heating rate. There is also control over the parameters of the solute such as its pH value, concentration and the type of solute. As there are a number of processing variables which can be controlled during hydrothermal synthesis, it can be hybridized with several other processes to obtain highly crystalline products with narrow size distribution, high purity and low

Table 13.2 Materials used as reactor linings

Material	Temperature (°C)	Solutions	Remarks
Silver	600	Hydroxides	Recrystallization (gradual) and dissolution (partial)
Gold	700	Hydroxides, sulphates	Dissolution (partial) in hydroxides
Platinum	700	Hydroxides, chlorides, sulphates	Get Blacken in chlorides in presence of sulphur ions. Dissolution (partial) in hydroxides
Copper	450	Hydroxides	Reduction of corrosion in presence of fluoride ions as well as organic compounds
Titanium	550	Chlorides, hydroxides, sulphates, sulphides	Corrosion in NaOH solution greater than 25% and in NH ₄ Cl solution greater than 10%
Tantalum	500	Chlorides	Corrosion starts in NH ₄ Cl solution 78%
Armco iron	450	Hydroxides	Oxidation (gradual) producing magnetite
Graphite	450	Sulphates	Pyrolytic graphite most suitable for linings
Teflon	300	Chlorides, hydroxides	Poor thermal conduction

aggregation. Lots of work has been reported where hydrothermal synthesis has been hybridized with microwaves, electrochemical process, ultrasound, mechanical milling, optical radiation, hot-pressing and many other processes to enhance the quality of product.

13.6.1 Microwave-Assisted Hydrothermal Processing (MAH)

Microwaves, a component of the Maxwell's rainbow are short wavelength radio-waves in the gigahertz (GHz) range. Under the influence of the oscillating electric field of the electromagnetic wave, the charges within the sample execute forced oscillation and are polarized. Microwaves enhance crystallization kinetics by one to two orders of magnitude with respect to standard hydrothermal processing. Different materials have energy levels differently spaced hence they interact with microwaves differently. Their loss factor or conversion efficiency determines the amount of electromagnetic energy that will be converted into heat. So for efficient and rapid heating, reaction medium with high microwave absorbing ability should be selected. The microwave-assisted hydrothermal method combines the merits of microwave and hydrothermal methods, thereby reducing the reaction time to few minutes or few hours as compared to that in a purely hydrothermal method where reaction time ranges from several hours to several days. Among many experimental observations, one is by Xu et al. (2004) who synthesized a high quality pure hydroxy-sodalite zeolite membrane on the support of α -Al₂O₃ by microwave-assisted hydrothermal method and reported the synthesis of hydroxy-sodalite zeolite membrane within 45 min compared to 6 h of synthesis time by the conventional hydrothermal method.

Thus compared with conventional hydrothermal method, microwave-assisted hydrothermal synthesis has emerged as a novel heating model in material science due to its rapid volumetric heating, low reaction temperature, homogeneous thermal transmission, low thermal gradients and the phase purity with better yield. This method is promising for fabricating nanomaterials with various morphology viz. nanowires, nanorods, nano-needles and it is generally a low-cost process for the bulk production of nano- and micro-structures.

This method is used mostly for synthesis of ceramic powders. Many groups have reported on the successful synthesis of ceramics by MAH technique like, Newalkar and Komarneni (2002) synthesized micropore-free hydrothermally stable mesoporous silica SBA-15 under microwave hydrothermal conditions at 373 K for 120 min. Bondioli et al. (2005) prepared nanocrystalline Pr-doped ceria powders with uniform sizes of 25–30 nm within 1 h by microwave-assisted hydrothermal route. Komarneni et al. (1993) prepared BaTiO₃, SrTiO₃, Ba_{1/2}Sr_{1/2}TiO₃, BaZrO₃, SrZrO₃, PbZrO₃, and Pb(Zr_{0.62}Ti_{0.48})O₃; ceramics and ZnO rod-assembled microspheres were successfully synthesized by Zhu et al. (2011). They concluded that ZnO prepared by MAH technique had an excellent optical property and higher

photocatalytic activity and displays good recyclability and stability than that of ZnO prepared by conventional hydrothermal technique. In most cases, ionic solvents are used as the medium for the hydrothermal reaction in the presence of microwaves because it helps to reduce the processing temperatures for various kinds of the ceramic materials. Thus, the synthesis of ferrites at low temperature is also possible by this process. ZnFe_2O_4 nanoparticles, iron hydroxyl phosphates ($\text{NH}_4\text{Fe}_2(\text{PO}_4)_2\text{OH}\cdot 2\text{H}_2\text{O}$) nanostructures, $\alpha\text{-FeOOH}$ hollow spheres, $\beta\text{-FeOOH}$ architectures and $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were prepared successfully by Tadjarodi et al. (2014) and Cao et al. (2010), respectively. Other synthesized materials are SnO_2 microspheres (Dong et al. 2008) and Bi_2O_3 (Schmidt et al. 2018), etc.

13.6.2 Sol-Gel-Hydrothermal (SG-HT) Method

The sol-gel method is well known as one of the versatile methods to synthesize inorganic compounds, including metal oxides, complex oxides, chalcogenides and many more. The Royal Society of Chemistry explains the sol-gel method as the process of the settling of (nm sized) particles from a colloidal suspension onto a pre-existing surface, resulting in ceramic materials. The desired solid particles (*e.g.* metal alkoxides) are suspended in a liquid, forming the “sol”, which is deposited on a substrate by spinning, dipping or coating, or transferred to a mould. The particles in the sol are polymerized by partial evaporation of the solvent, or addition of an initiator, forming the “gel”, which is then heated at high temperature to give the final solid product.

The sol-gel method is a promising low-energy method; however, in the case of powder syntheses, a subsequent heating process is often needed to obtain the desired compounds, and agglomerated nanoparticles are usually obtained. On the other hand, the sol-gel method combined with hydrothermal method (SG-HT) is capable of synthesizing microstructure-controlled nanoparticles at a lower temperature. The experimental procedure, divided in two major heads, sol-gel preparation and hydrothermal treatments are as depicted in Fig. 13.6.

Few reports on SG-HT are listed here. Valencia et al. (2010) synthesized titanium dioxide nanoparticles by the sol-gel method followed by a hydrothermal treatment using tetraisopropyl orthotitanate (TIOT) and 2-propanol. Gong et al. (2008) reported the synthesis of carbon-coated $\text{Li}_2\text{FeSiO}_4$ material through hydrothermal-assisted sol-gel process by adding sucrose to the synthetic precursor. The $\text{Li}_2\text{FeSiO}_4$ so obtained showed large reversible capacity under high rate charge and discharge and excellent capacity retention. Ueno et al. (2015) synthesized silver-strontium titanate hybrid nanoparticles by sol-gel-hydrothermal method. Fuentes et al. (2010) also prepared strontium titanate, SrTiO_3 , using the sol-gel-hydrothermal reaction of TiCl_4 and a SrCl_2 solution in an oxygen atmosphere.



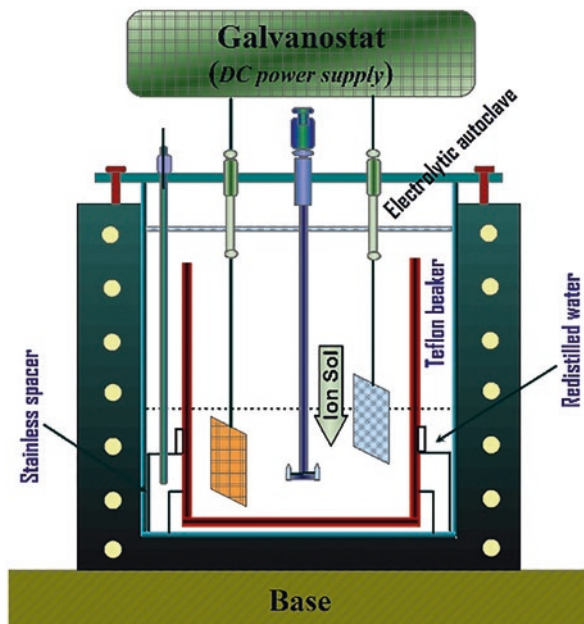
Fig. 13.6 Sol-gel combined hydrothermal method

13.6.3 Hydrothermal-Electrochemical Synthesis (HE)

Hydrothermal-electrochemical technique combines hydrothermal process with electrochemical method and results in deposition of crystalline thin films on metallic substrate directly from nanostructured products of hydrothermal reaction. It is particularly important in the case of crystalline oxide products, which cannot precipitate out of solution in the absence of an applied electric potential.

Hawkins and Roy (1962) introduced electrodes into a hydrothermal bomb and studied the influence of an electric field on the synthesis of kaolinite. They showed a very substantial effect ($>100\text{ }^{\circ}\text{C}$) of lowering the crystallization temperature of kaolinite. Yoshimura popularized this concept by extending it to the synthesis of electroceramics, particularly perovskite-type oxides. Figure 13.7 shows the schematic diagram of the autoclave designed in Yoshimura's laboratory at the Tokyo Institute of Technology, Japan, for the hydrothermal-electrochemical reactions, using three-electrode technique of Bard et al. (1980).

Fig. 13.7 Schematics of the electrochemical cell with dc power supply for the hydrothermal-electrochemical method



This has a provision to measure potentials of electrodes in aqueous solutions at high temperatures and pressures on a thermodynamically meaningful scale, regardless of the electrolysis conditions. Yoshimura's group has worked extensively on this and successfully prepared perovskite-type titanates such as SrTiO_3 , CaTiO_3 and BaTiO_3 thin films up to several micrometres in thickness, almost linearly, at fairly lower temperatures ($<90^\circ\text{C}$) (Suchanek and Yoshimura 1998; Yoshimura et al. 1999). They have also studied the growing interface, the transport mechanism of the atoms across the growing film without concentration gradients. It also enables fabrication of ceramic super lattices. Villegas and Stickney (1992) and Colletti et al. (1998) grew monomolecular or atomic layer films of GaAs, CdTe, CdSe and CdS semiconductors, equivalent to molecular beam epitaxial, using aqueous solutions instead of a vapour phase for transport of growth species.

Basca et al. (1992) also crystallized polycrystalline films of cubic BaTiO_3 on Ti metal substrates by electrochemical, hydrothermal and electrochemical-hydrothermal reaction of a Ti metal with a saturated solution of $\text{Ba}(\text{OH})_2$ in the temperature range $80\text{--}200^\circ\text{C}$. The electrochemical-hydrothermal combination reduced the reaction time to only 30–45 min. The reduced reaction time is desirable as they observed that crystallinity decreased with extended time of reaction for a given temperature.

13.6.4 Mechanochemical-Hydrothermal Synthesis (MCH)

The mechanochemical-hydrothermal synthesis often termed as wet mechanochemical synthesis utilizes an aqueous solution as a milling medium. The aqueous solution actively participates in the mechanochemical reaction, thereby accelerating dissolution, diffusion, adsorption, reaction rate and crystallization (Yoshimura and Suchanek 1997). For the mechanochemical-hydrothermal processing, there is no need for a pressure vessel and external heating as pressure can be applied at room temperature by milling equipment, and energy required for reaction is provided in the form of mechanical energy. Thus, mechanochemical-hydrothermal technique jointly uses the mechanism of hydrothermal and mechanical alloying. Collision between the balls, between balls and wall (present inside milling instrument) and their mutual friction creates localized zones of high temperature and high pressure and the heat generated adiabatically raises the temperature of the slurries as high as 450–700 °C (Kosova et al. 1997).

Ceramics such as PbTiO_3 and hydroxyapatite have been made with this approach. Shuk et al. (2001), Riman et al. (2002) and Abdel-Aala et al. (2008) have synthesized nano-crystallite hydroxyapatite by this method. Although the mechanochemical method appears promising for the synthesis of ceramic precursors, it has some possible disadvantages like high energy consumption and possible contaminations from the milling media. In addition, control of particle size, morphology and aggregation is a challenge for this method since MC-HT method fails to regulate rates of nucleation, growth and ageing unlike conventional hydrothermal technologies.

13.6.5 Ultrasound-Assisted Hydrothermal Crystallization (UAH)

Under the ultrasound-assisted hydrothermal crystallization, often known as sonochemical technique, molecules undergo chemical reactions due to the application of powerful ultrasound radiation (20 kHz to 10 MHz). Ultrasound is known to accelerate the reaction kinetics by as much as two orders of magnitude owing to acoustic cavitation (Yamakov et al. 2004). Besides accelerating the reaction rate, UA-HT also yields polycrystalline thin films with smooth surface, thereby reducing the possibility of electrical breakdown when subjected to electric field. The sonochemical environment is also considered to alter molecular chemistry and enhance mass transport (Peters 1996). The schematic diagram of the ultrasonically assisted hydrothermal system has been illustrated in Fig. 13.8.

This method, initially proposed for the synthesis of iron nanoparticles, is nowadays used to synthesize different metal oxides. The sonochemical technique involves passing sound waves of fixed frequency through slurry or solution but this arrangement is difficult to achieve as hydrothermal method is carried out in a sealed stain-

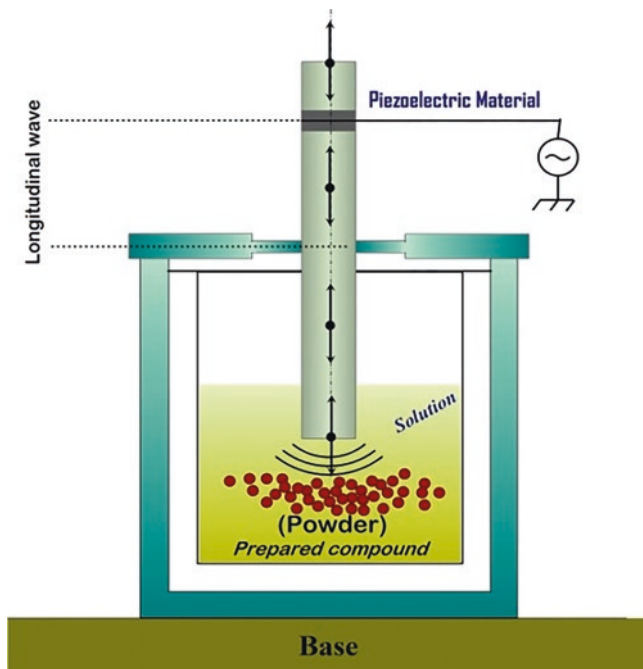


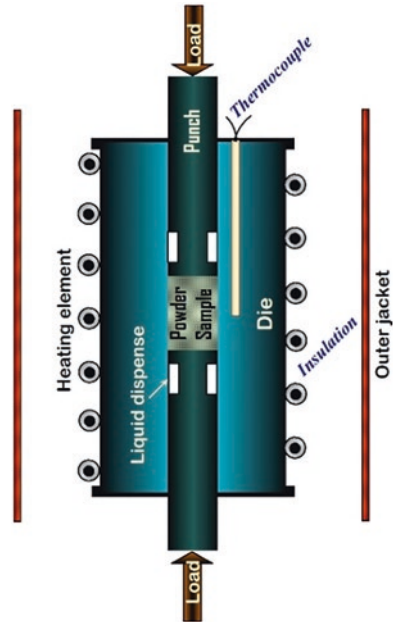
Fig. 13.8 Schematics of the ultrasonically assisted hydrothermal system

less-steal container under high pressure and high temperature. Ishikawa et al. (2008) constructed a reaction container with an ultrasonic transducer integrated into the lid of an autoclave for synthesis of KNbO_3 piezoelectric ceramics and ultrasonically assisted hydrothermal PZT thin films. They observed noticeable effectiveness— increase in the reaction rate of the KNbO_3 powder and smoothening in the surface of the PZT thin film. They further enhanced the device by improving the vibration speed even under high-temperature conditions and examined its effect on PZT thin film deposition and $(\text{K},\text{Na})\text{NbO}_3$ powder fabrication.

13.6.6 Hydrothermal Hot-Pressing (HHP)

Hydrothermal Hot-Pressing (HHP) technique is a processing route for producing a ceramic body at relatively low temperatures typically below 300°C . This technique is applied to solidify many kinds of the materials such as silicate glass, titania, calcium carbonate and hydroxyapatite (Hosoi et al. 1998). The hydrothermal hot-pressing method (Fig. 13.9) has two characteristics: continuous compression of samples under hydrothermal conditions and space for water retreat. Compression accelerates compaction of starting powder and prevents development of cracks by shrinkage. Compaction depends on the rate at which water can be expelled from the

Fig. 13.9 Schematic of autoclave for hydrothermal hot-pressing



starting powder. The hydrothermal hot-pressing method requires the space for water retreat, into which water included in the starting powder is released. Without the space, water exists in pore space of the starting powder and hinders compaction of the powder. During the hydrothermal treatment, mass transport leading to densification occurs mostly by a dissolution precipitation mechanism. Low processing temperatures enable the incorporation of organic components that can further improve the mechanical strength of the ceramics.

13.6.7 Hydrothermal–Photochemical Synthesis (HP)

Photochemical synthesis is used to describe a chemical reaction caused by absorption of light. Photochemical reactions proceed differently than temperature-driven reactions. Photochemical paths access high-energy intermediates that cannot be generated thermally, thereby overcoming large activation barriers in a short period of time, and allowing reactions otherwise inaccessible by thermal processes. Adding optical irradiation to hydrothermal technique increases growth rates by an order of magnitude for ceramics and three orders of magnitude for metals (Tamir and Zahavi 1985; Itoh et al. 1991). Enhancement of the reaction rate can be attributed to temperature, diffusional enhancement due to light induced thermal gradients that micro-stir the solution and/or photo-chemistry. Examples of ceramics synthesized by the hydrothermal–photochemical include thin films of Ni-, Zn-, Co- and Mn-ferrites, Tl_2O_3 and Fe_3O_4 .

13.7 Merits of Hydrothermal Methods

Like any other conventional synthesis techniques, the hydrothermal technique also has its merits and demerits. They are listed as under:

- The hydrothermal synthesis is particularly suitable for the growth of large good-quality crystals of desirable composition, size, shape and crystal structure. Crystals of controlled shape, size and composition are essential as they strongly influence magnetic, electric, optic and other properties of the sample. This method is especially of great importance to those industries (like pharmaceuticals, paint industry, etc.) whose starting material is powder in raw form because hydrothermal synthesis yields products with controlled size morphology.
- Under hydrothermal conditions, since the properties of water such as vapour pressure, density, surface tension, viscosity, and ionic product can be greatly changed, it can decrease the reaction temperature of systems; prepare crystalline products with narrow size distribution, high purity and low aggregation.
- Hydrothermal synthesis is very useful technique when it comes to defect (crystal defects: stress defects, Schottky defects) minimization. For example, tungstates of Ca, Ba and Sr synthesized at room temperature by a hydrothermal method do not contain Schottky defects usually present in similar materials prepared by solid-state reaction technique at high temperatures, which results in improved luminescent properties. Added advantage of hydrothermal technique is proper stoichiometry due to the non-attainment of volatilization temperature and microcrack-free samples, as phase transition is not involved at low temperatures.
- With this method, it is possible to grow crystals of compounds with high melting points at lower temperatures.
- Materials, which have a high vapour pressure near their melting points, can be grown by the hydrothermal method.
- Compounds with elements in oxidation states that are difficult to obtain (like compounds of transition metal) can be obtained inside a pressurized vessel by the hydrothermal method.
- Low temperature phases viz. quartz, berlinite and others can be easily achieved by hydrothermal technique.
- Under hydrothermal conditions as reaction takes place in a closed system, studies on phase equilibrium and the influence of temperature and pressure on phase boundary can be carried out.
- From the environmental perspective, hydrothermal methods are more environmentally benign than many other methods, thereby abiding by the rules imposed by European Union.
- A major advantage of hydrothermal synthesis is that this method can be hybridized with other processes like microwave, electrochemistry, ultrasound, mechano-chemistry, optical radiation and hot-pressing to gain advantages such as enhancement of reaction kinetics and increase ability to make new materials.

13.8 Demerits of Hydrothermal Methods

The hydrothermal technique is challenged at two major fronts:

- The need of expensive autoclaves.
- As reaction takes place in a closed system, it is impossible to observe and monitor the growth process of materials.

13.9 Comparison of $\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ Synthesized by Solid-State Reaction Method, Hydrothermal Technique and Mechanical Alloying

With increasing working population, rising household incomes and increasing disposable income, the global consumer electronics market has thrived imposing high demand of microelectronic, opto-electric and magneto-electric devices. Most of these devices employ ceramics, which are usually lead based, and have a short service life, often ending up in a landfill within a few months or years. Attempts to recycle the lead in these products have not been successful. The disposed lead in the environment has subsequent effects on the ecosystem and needs to be addressed. A large body of work has been reported in the last decade on the development of lead-free piezoceramics in the quest to replace lead-based ceramics (Cross 2004; Rödel et al. 2009; Takenaka and Nagata 2005; Shrout and Zang 2007; Lau et al. 2008). It is observed from the literature that sodium potassium niobate (Saito et al. 2004; Fuyuno 2005; Kimura and Ando 1999; Wolny 2004), bismuth sodium titanate (Prasad et al. 2007; Sakata and Masuda 1974; Dorcet et al. 2008; Troiliard and Dorcet 2008; Nagata et al. 2004) and related materials are potential lead-free materials.

In recent years, complex perovskites with nominal chemical formula $\text{A}(\text{Fe}_{1/2}\text{B}_{1/2})\text{O}_3$ (A: Ba, Sr and Ca; B: Nb, Ta and Sb) have attracted much attention because of their giant dielectric (10^3 – 10^5) response over a wide temperature and frequency interval (Wang et al. 2007a, b; Raevski et al. 2003; Chung et al. 2004; Homes et al. 2001; Bhagat and Prasad 2010; Roy et al. 2017). Among these perovskites barium iron niobate, $\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (abbreviated hereafter as BFN) and barium iron tantalate, $\text{Ba}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (abbreviated hereafter as BFT) bulk and nano have been synthesized by different researchers by variety of techniques, like solid-state reaction method, hydrothermal method and mechanical alloying. Some of the methods are biased to performance and neutral to the environment. The hydrothermal technique is one, which is in line with the development of ecologically benign, “green” compounds.

Reaney et al. (1994) first prepared BFN by solid-state reaction method. Saha and Sinha (2002), Raevski et al. (2003), Chung et al. (2004), Eitssayeam et al. (2006), Intatha et al. (2007, 2009) and Wang et al. (2007a, b) further investigated BFN but

all synthesized it by high-temperature reaction method. Charoenthai et al. (2008) for the first time synthesized BFN powders by microwave synthesis. Microwave-assisted sol-gel synthesis of BFN ceramics for MLC (Multilayer Capacitor) applications was carried out by Sonia and Kumar (2017). Köferstein and Ebbinghaus (2017) prepared BFN by a low temperature aqueous synthesis. In a very recent work BFN ceramic powder with average size 12–20 nm were synthesized mechanochemically by Bochenek et al. (2018). A relatively new approach for obtaining nanosized particles of $\text{Ba}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ and $\text{Ba}_{0.06}(\text{Na}_{1/2}\text{Bi}_{1/2})_{0.94}\text{TiO}_3$ was reported by Mahto et al. (2016, 2018) which can be epitomized for BFN nanoparticles too. The advantage behind this method is the surety of phase formation. In this approach, the ceramics are first formed by solid-state reaction method ensuring proper phase and then milled to nanosize. As phase formation takes through solid-state reaction method so reduction to nanoceramics involves less milling hour, thereby reducing energy consumption and the possibility of contamination.

Here we provide a comparative study of BFN prepared by solid-state reaction method, hydrothermal method and mechanochemical method. In a particular work polycrystalline BFN was prepared by Bhagat and Prasad by solid-state reaction method (Bhagat and Prasad 2010), and BFN nano powders were prepared by a low temperature aqueous synthesis by Köferstein and Ebbinghaus (2017), whereas BFN ceramic powder were synthesized mechanochemically by Bochenek et al. (2018). An attempt has been made to show the experimental parameters and involved steps by a flowchart (Fig. 13.10) in the above-mentioned synthesis techniques. Figure 13.11 shows the diffraction peaks and the SEM images for bulk and nano BFN ceramics.

BFN samples were prepared by Köferstein and Ebbinghaus (2017) by reaction of Ba^{2+} , Fe^{3+} and Nb^{5+} reactants in boiling NaOH solutions with different concentrations (2, 6, 8, 10 and 14 mol/L of NaOH). Detailed characterization was carried on the

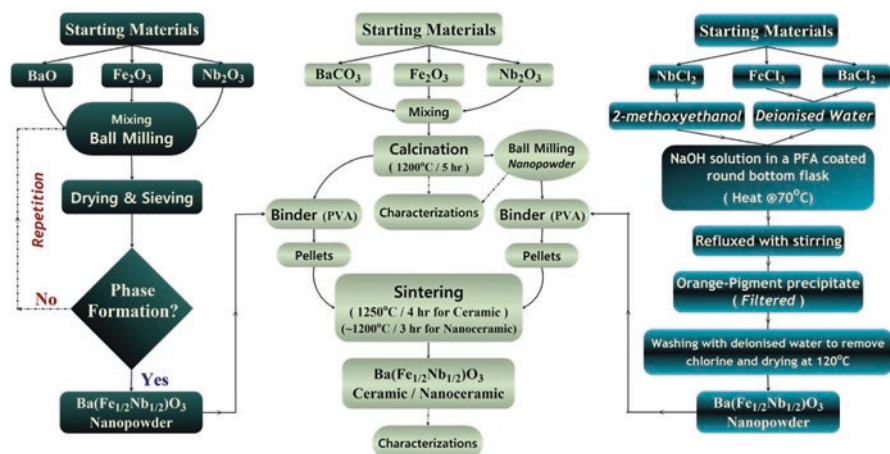


Fig. 13.10 Comprehensive synthesis mechanism of $\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ by different techniques

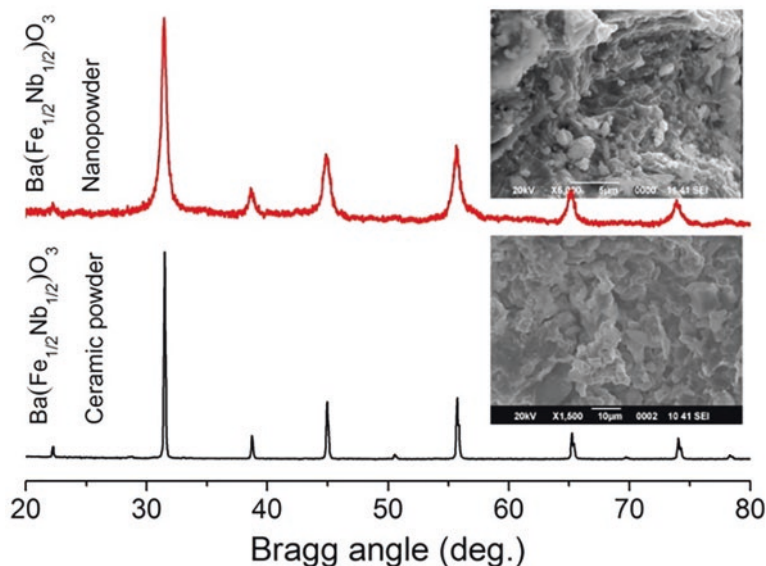


Fig. 13.11 Diffraction peaks and the SEM images for bulk and nano BFN ceramics

as-prepared powder BFN-8M sintered at 1000 °C, as below this concentration impurity % was more and above this concentration formation of pure phase took place but with increase in particle size. The average crystallite size was calculated to be 15 nm and the root-mean-square strain was found to be 1.7×10^{-3} . TEM images showed spherical particles in the range between 9 and 25 nm. The dielectric constant and loss tangent at room temperature at 1 kHz frequency for the BFN-8M sintered at 1200 °C is reported to be 5.8×10^3 and 0.5 (approximately) with activation energy ≈ 5 eV.

Bochenek et al. (2018) prepared BFN nanoceramics by high-energy ball milling. After 20 h of milling of the mixture of the starting powders pure BFN perovskite phase has been recorded. As the flowchart depicts BaO being one of the starting powder, no calcination step was required for phase formation. The average crystallite size was found to be nearly 16 nm (approximately) for the the 20 h milled BFN sample. The average grain size for the 20 h milled sample was found to be 12.8 μm through SEM images. The final parameters of the obtained ceramics suggested that the optimal high-energy milling time is 60 h. The dielectric constant and loss tangent at room temperature at 1 kHz frequency for the 60 h milled BFN nanoceramics is reported to be 6×10^4 and 0.5. The phase transition temperature at 1 kHz was reported to be 254 °C.

The values of average crystallite size and lattice strain, reported by Bhagat and Prasad (2010), respectively, are 84 nm and 0.0008. The low value of lattice strain in solid-state reaction method might be due to the fact that the synthesis procedure does not impose much constraint in the formation of compound as is generally

found in case of extensive ball milling technique. Grains of unequal sizes (2–5 μm) were found to be distributed throughout the sample. Dielectric constant near to room temperature (20 $^{\circ}\text{C}$) was found to be 3699. The value of activation energy was estimated to be 0.327 eV at 1 kHz.

Compared with BFN ceramics obtained by the mixed-oxide method, the soft-chemistry synthesis and high-energy ball milling lead to ceramics: with up to one order of magnitude, higher permittivity values exhibit lower temperature dependency and higher activation energy. The activation energy is higher in chemical route, which reflects the fact that the crystallite growth process starts only at high temperatures in these processes.

13.10 Conclusion

We started with the sentence “Nanoparticles: Last in the line above the atom, the most difficult to find, and the hardest to learn from”. Indeed, a true nanoscale control of matter is more difficult than its conception. Then also our understanding of the laws of nature at nanoscale using quantum physics is still impressive. Keeping in mind the generations to come, hydrothermal synthesis is a suitable method for preparing nanoparticles which find its application in all streams of life, from healthcare to manufacturing, space travel to improving our environment. The hydrothermal technique can be easily hybridized with other synthesis techniques to reduce the reaction time and efforts, yield products having desired properties, enhance the quality of product, etc. In the present study a technologically important material, BFN nanopowder grown hydrothermally, was considered to establish these facts.

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Chapter 14

Hydrothermal Synthesis of Hybrid Nanoparticles for Future Directions of Renewal Energy Applications



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14.1 Introduction

The term “hydrothermal” was first coined by a geologist Sir Roderick Murchison (1792–1781) to illustrate the changes observed in the earth’s crust by the formation of various rocks and minerals due to action of water at high temperature and pressure. The formation of beryl crystal in single crystal structure is the pertinent example of nature using hydrothermal origin whereas as the quartz is the example of manmade crystal using this technique. Upon the observation of great structural control and manipulation, this process was widely introduced in nineteenth century for the research purpose. R.W. Bunsen in 1839, first time used this process to prepare Barium (Ba) and Strontium carbonate at temperatures above 200 °C and pressures above 100 bars. Thereafter, E. Schafhautl in 1845 grew the quartz crystals of silicic acid in small dimension using autoclave hydrothermal decomposition (Lalena et al. 2008). This process was further comprehensively verified (Roy 1994; Roy and Tuttle 1956) on clay mineral and synthesis of zeolite families of various sizes ranging between 7 and 14 Å for oxide phase transformation study and creation of various vacancy disordering. Afterwards, this technique has been considered as one of the most versatile techniques which can produce a variety of fine particles of different materials in various shapes and structures.

In early 1990s, the hydrothermal process was extensively adopted by the researcher for processing of fine to ultra-fine particles with a controlled size and

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morphology. The easy control over the sizes, shapes, and morphologies dragged it into the era of new technology, namely “Nanotechnology” as the major materials processing tools. The control over the particles manipulation from sub-micrometer to nanosize allows better understanding over the relevant technological applications. The phenomenological new terminology “Nanotechnology” was introduced by the Eric Drexler (1986) in his book *Engines of Creation*, where the emphasis was given on the manipulation of individual atoms and molecules to build structures to complex atomic specifications. Perhaps, the concept of nanotechnology extracted from the landmark lecture on “*There’s Plenty of Room at the Bottom*” delivered by the Richard Feynman (1959), physicist.

The research interest in materials having small size close to nanosize (1–100 nm) in one of the spatial dimensions is grown due to the fact that small-sized system exhibits completely new properties from their bulk counterparts, and these properties vary with size and/or shape of the particles. The properties include optical, magnetic, and electronic which may be important applications in material technologies like microelectronics, catalytic systems, hydrogen storage, ferrofluids, chemical nanosensors, etc. Nanomaterials have been extensively investigated during the last decade due to their wide variety of applications. It is observed that field of nanomaterial synthesis is very dynamic. Many process such as gas condensation, chemical vapor synthesis, mechanical attrition, chemical precipitation, sol-gel technique, electrodeposition, and some other methods widely used are molecular beam epitaxy, ionized cluster beam, liquid metal ion source, consolidation, sputtering, and gas aggregation of monomers chemical precipitation in presence of capping agents, reaction in micro-emulsions, and auto-combustion are commonly used techniques for synthesis of nanophosphors. Table 14.1 shows the impact of the various processes on the morphology, quality of product, reaction control, etc., whereas Table 14.2 presents the advantages of the hydrothermal process over other processes.

Table 14.1 Comparison of various synthesis processes

S. no.	Synthesis techniques	Structural control	Morphology control	Reactivity	Particle size (nm)
1.	Solid state technique	Poor	Poor	Poor	≥ 20
2.	Co-precipitation technique	Good, high	Moderate	Good, high	≥ 10
3.	Spray technique	Excellent	Moderate	Good, high	≥ 10
4.	Emulsion synthesis	Excellent	Excellent	Good, high	≥ 10
5.	Spray pyrolysis technique	Excellent	Excellent	Good, high	≥ 10
6.	Sol-gel synthesis	Excellent	Moderate	Good, high	≥ 10
7.	Hydrothermal technique	Excellent	Good, high	Good, high	≤ 10

Table 14.2 Comparative analysis of the different synthesis process versus hydrothermal methods

S. no.	Hydrothermal process	Other process
1.	Hydrothermal process is the self-purifying process and chemicals required very low purity of acetates, isopropoxides, oxides, nitrates, and chlorides of the elements	Solid state process requires high purity chemical of the oxides, acetates, isopropoxides, and oxy-nitrates
2.	Inexpensive precursor materials are useful for this process. The product quality is better than any other processes	Other processing methods required high purity precursor chemicals to produce quality products
3.	This process works at very low temperature. In most cases, it works below 200 °C which minimizes the problems related to the stoichiometry control for the materials have volatile nature. Here, no calcination or annealing is required for the final product in various cases	Other methods produce amorphous materials as a product that needs the high temperature calcination for a couple of hours
4.	Hydrothermal process is easy and safe for samples preparation because it is an environment-friendly method compared to others. This method provides versatile options for the synthesis of the multifunctional semiconductor and ceramic materials like electronic ceramics, bioceramics, catalyst supports, membranes, and ceramics with electronic, magnetic, and optical properties	Other methods are not so versatile for the multifunctional semiconductor and ceramic materials like electronic ceramics, bioceramics, catalyst supports, membranes, and ceramics with electronic, magnetic, and optical properties
5.	Because of cost-effective and reproducible nature of production of high-quality ceramic powders on a large scale, it can be scaled up to meet the industrial requirement or demands	Low quality product restricts the scaling up of the sol-gel and co-precipitation techniques
6.	Hydrothermal process allows designing the particles in various shapes and sizes in shorter reaction times over the good control on the reaction process	Other methods such as sol-gel and co-precipitation have less control on the size and shape/morphology of the particles

Thanks are due to the advancement in the technologies which led the researchers to understand the hydrothermally grown nanosized particles, their formation process and their control in order to get the desired properties to such nanomaterials. It is therefore hydrothermal technology considered as one of the most apprised techniques in the field of nanotechnology. Presently, the research reports forecast that in coming future, the hydrothermal technology may take a key place in several interdisciplinary branches of science and technology as well as shall work as bridge among the important technologies including nanotechnology, biotechnology, sensor technology and geo-technology, and advanced materials technology. Thus, it enriches that the hydrothermal processing of advanced materials is a highly interdisciplinary technique that is commonly used by materials scientists, hydro-metallurgists, physicists, engineers, chemists, ceramists, biologists, and geologists. Figure 14.1 shows various branches of science and technology which utilize the hydrothermal process as a source of materials development.

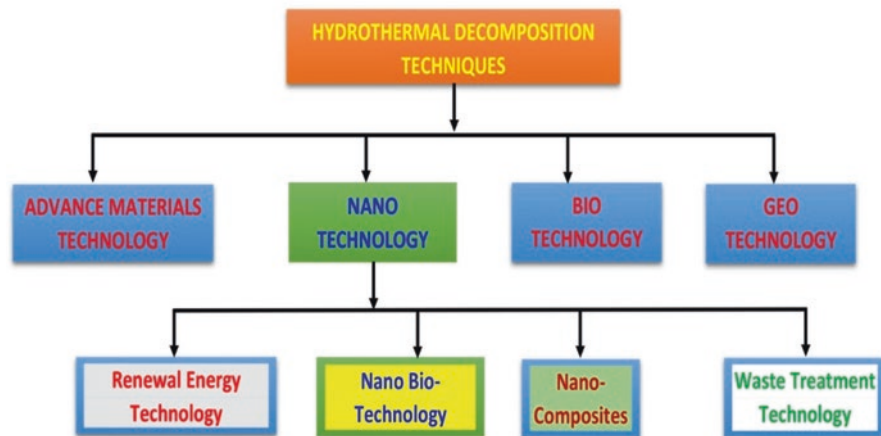


Fig. 14.1 Application of hydrothermal process in various science and technology fields

In addition to the processing of nanomaterials, it offers distinct advantages due to good control over the diffusivity in a strong solvent medium in a closed system. It is highly required for the case of nanomaterials especially of the functional materials because of the physico-chemical characteristics of nano-systems. As the size is reduced to the nanometer range, the materials exhibit peculiar and interesting mechanical and physical properties viz. improved mechanical strength, enhanced diffusivity, higher specific heat, and electrical resistivity compared to their conventional coarse grained counterparts due to a quantum size effect (Yamakov et al. 2004). With continuous growing demand for composite nanostructures, the hydrothermal technique also offers a unique option for coating of various polymeric compounds on metals, polymers, and ceramics as well as for the fabrication of powders or bulk ceramics. Therefore, it is now considered as a frontline technology for the processing of advanced materials for nanotechnology application. Nowadays, the conventional hydrothermal methods as well as its variants have emerged as a versatile synthesis option for the preparation of multifunctional ceramics materials for electronic, bio, magnetic, catalysts, optical, and other properties (Ortiz-Landeros et al. 2012).

14.2 Types of Hydrothermal Method

Unique advantage of hydrothermal synthetic process provides the numerous ways for technological hybridization in order to make new materials for high-technology applications. To this end, various upgradations in the hydrothermal process are done in combination with other advance processes. Presently, this process is combined or hybridized with the different sources of energies such as microwaves, sol-gel, electrochemistry, ultrasound, mechano-chemistry, optical radiation, and hot-pressing.

The working process of these hybrid techniques are briefly discussed in Chap. 13 for the synthesis of the advanced nanomaterials and their composites.

14.3 Hydrothermal Processing Chemistry of Advanced Materials for Nanotechnology Applications

Understanding of the chemistry of materials in hydrothermal processing is considered as the key features for the purpose of designing new materials for advance technology. The process chemistry includes the understanding of the solvent chemistry behavior such as structure at critical, dielectric constant, pH variation, viscosity, coefficient of expansion, and density of materials in hydrothermal process conditions with respect to temperature and pressure dependency. Using this process, mostly the solubility, stability, yield, dissolution, and precipitation reactions of materials are studied because the analysis of the change in intermediate kinetics of the intermediate phase formation is absent. Therefore, in 1950–60s, the synthesis of zeolites in presence of temperature and pressure storm the importance of the crystallization kinetics of the materials and the ability to empirically define the essential roles of various parameters such as temperature, pressure, precursor, and time involve in crystallization kinetics of various compounds (Byrappa and Adschiri 2007). Accurate understanding on the role of these parameters for the formation of solution species, solid phases, and the rate of their formation requires to explore the appropriate modeling approach. In this connection, the rational engineering approach is developed to understand the intermediate conditions of the process and also further improve the process development. The steps involved in this approach are (1) computing of thermodynamic equilibria as a function of chemical processing variables, (2) generation of equilibrium diagrams to access the process variable for the points of interest, (3) plan hydrothermal experiments to authenticate the computed diagrams, and (4) utilization of the processing variables for controlling the reactions and crystallization kinetics. Using such a modeling approach, theoretical stability field diagrams or yield diagrams are designed to obtain yield close to 100%. Considering the materials product is in pure phase, the yield (Y) of materials can be expressed in the form of

$$Y_i = \frac{100(m_i^x - m_i^y)}{m_i^x} \%$$

here m^x and m^y are the input and equilibrium molar concentrations of the species, respectively, for the i th atoms. As a result, this approach successfully provides the control over the phase purity, particle size, size distribution, and particle morphology by predicting the optimal synthesis conditions (Lencka and Riman 2003; Gersten 2003; Riman et al. 2002).

14.4 Instrumentation Requirement for the Hydrothermal Processing of Nanomaterials

As the reaction are being carried out at high temperature and pressure in a closed vessel in hydrothermal processing, the requirement or selection of materials to design the equipment known as autoclave, reactor, pressure vessel, or high pressure bomb is very important. Designing an ideal hydrothermal vessel is supposed to be a tough job and perhaps difficult because each experimental conditions has different objectives and tolerance limits. In most practical cases, the materials used for an ideal hydrothermal autoclave should have the following characteristics such as unresponsiveness to acids, bases and oxidizing agents, simplicity of assembly and disassembly, sufficient length for desired temperature gradient, leak-proof capabilities at operating temperature and pressure, and quality to sustain high pressure and temperature during experiments for long periods without damage. Considering these requirements, materials used for the fabrication are glass cylinder, quartz cylinder, and alloys, such as austenitic stainless steel, iron, nickel, cobalt-based super alloys, and titanium and its alloys. The commonly used reactors in the hydrothermal processing of advanced nanomaterials are general purpose autoclaves, morey type flat plate seal, stirred reactors, cold-cone seal tuttle-roy type, TZM autoclaves, batch reactors, flow reactors, microwave-hydrothermal reactors, mechano-chemical-hydrothermal, piston cylinder, opposed anvil, and opposed diamond anvil. The parameters to be considered for the selection of a suitable reactor are

1. Experimental temperature and pressure.
2. Corrosion resistance behavior for a given solvent or fluid at operating pressure-temperature.

14.5 Hydrothermal Synthesis of Advanced Nanomaterials

The nanomaterials are well recognized nowadays because of their unique properties such as mechanical, chemical, physical, thermal, electrical, optical, magnetic, and also specific surface area properties. Based on such properties, it is known by several names such as nanostructures, nano-electronics, nano-photonics, nano-biotechnology, and nano-analytics. In the last one decade, a large variety of nanomaterials and devices with new capabilities have been generated employing nanoparticles based on metals, metal oxides, and semiconductors including the II–VI and III–V compounds, silicates, sulfides, hydroxides, tungstates, titanates, carbon, zeolites, ceramics, and a variety of composites. Here, some of the forms of the nanomaterials are discussed.

14.5.1 *Metal Nanoparticles*

Owing to the fundamental technological properties, noble metals like Au, Ag, Pt, Co, Ni, and Fe, metal alloys such as FePt, CoPt, and multilayers of Cu/Co, Co/Pt have drawn considerable attention of the researchers to think in new ways of the utilization of these materials in different sizes and morphology (Forster and Antonietti 1998; Zhu et al. 2003; Puentes et al. 2001; Xie et al. 2005) because of the inherent properties of metal nanoparticles strongly governed by their size, shape, and structure. More often, the synthesis of these metals was done by using both the hydrothermal and hydrothermal-supercritical water techniques in order to study the crystal growth process and shape control. Zhu et al. 2003 have reported the mild hydrothermal reactions process for the synthesis of silver nanoparticles in dendrite nanostructures in presence of the anisotropic nickel nanotubes as a reducing agent. The morphologies changed from dendrite to compact crystals were observed during the progress of the reaction from non-equilibrium to quasi-equilibrium conditions. The use of PVP surfactant instead of the nickel, the nanostructures silver were swapped by bulk particles. Xie et al. (2005) and Liu et al. (2005) have reported the hydrothermal synthesis of cobalt nanorods and nanobelts with and without surfactants. Cobalt nanorods with hcp structures was obtained at 90 °C with an average particle size of 10 nm diameter and 260 nm length (Liu et al. 2005) by using micro-emulsion with hydrothermal process. Similarly, Co nanobelts via a surfactant-assisted hydrothermal reduction process at 160 °C or 20 h have been reported by Xie et al. (2005). Liu et al. (2005) have reported a complex-surfactant-assisted hydrothermal route to ferromagnetic nickel nanobelts at about 110 °C in 24 h.

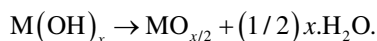
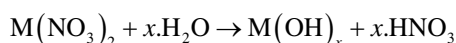
Recently, the synthesis of Ag, Au, Pd, In, Pt, Si, Ge, Cu, etc. nanoparticles via supercritical conditions reactions are becoming very popular due to its fast kinetics and rapid particle production quality with the shortest dwelling time. There are several reports on the preparation of nanoparticles under supercritical conditions reactions (Reverchon and Adami 2006; Kameo et al. 2015; Shah et al. 2001; McLeod et al. 2004). Similarly, the coating of nanocrystalline films of Cu, Ni, Ag, Au, Pt, Pd, Rh, etc. on silicon wafers for microelectronics, data storage, etc. were also done (Blackburn et al. 2001). It has been further extended to numerous other materials. Accordingly, the hydrothermal-solvothermal and hydrothermal-supercritical conditions offer unique advantages over the preparation of the metal nanoparticles over other conventional methods.

14.5.2 *Metal Oxide Nanoparticles*

Recent demands of mono-dispersed nano-dimension metal oxide particles such as TiO₂, ZnO, Fe₂O₃, Fe₃O₄, CeO₂, ZrO₂, CuO, Al₂O₃, Dy₂O₃, In₂O₃, Co₃O₄, NiO, and its composites with graphene, CNT, or metals with control morphology drawn considerable attention towards the processing techniques especially for the case of

hydrothermal process and its conditions for technological applications including catalytic, optical, drug delivery, magnetic imaging, hyperthermia, cancer therapy, photo-catalytic, luminescent, electronic, high-density information storage, etc. These applications mostly require particles of narrow size distribution with a high dispersibility in the appropriate dispersive medium depending on the technological requirement. Thus, to get the high dispersion of metal oxides mono-dispersed particles required a variety of modifications in the hydrothermal technique.

Adschiri et al. (Adschiri et al. 1992a, b, 2000, 2001; Hakuta et al. 1998a, b) described a continuous synthesis of narrow size metal oxide particles using metal nitrates and in presence of the supercritical water as the reacting medium. Here, the production of small size fine particles is because water rapidly dehydrates the metal hydroxides before the occurrence of the substantial growth of particles. The overall reactions involve a two-step process, i.e., hydrolysis of metal salts to metal oxides and its dehydration



In this process, rate of dehydration is controlled in such a way that the rate of reaction is hardly affected by diffusion growth process, resulting in small size particle formation. Additionally, the process also brought the negligible mass transfer because of the gas like viscosity and diffusivity of water in the critical region. Thus, the overall synthesis rate is significantly high. Moreover, if the temperature is introduced in the process, the reaction rate is also affected.

Recently, TiO₂ and its composites are extensively developed by a large number of researchers using the hydrothermal process for the energy harvesting applications because TiO₂ is non-toxic and chemically inert and produces maximum light scattering. In a most recent work, Singh et al. (2014) successfully prepared the ternary phase plasmonic photo-catalyst using hydrothermal process. The photo-catalyst includes graphene-Au-TiO₂ nano-system and is used for the production of hydrogen from photo-catalytic water splitting and control of environmental pollution through dye degradation in presence of simulated solar spectrum. The X-ray diffraction patterns of these nanocomposites are shown in Fig. 14.2. It is observed that the peaks shifted towards higher angles, which imply the reduction in inter-planer spacing after incorporation of Au. The Au peaks are observed in the sample containing Au contents 8.0 wt% in rGO-TiO₂. Transmission electron microscope (TEM) images of these composites are shown in Fig. 14.3.

The environmental pollution control through dye degradation process involves firstly the absorption of photons by TiO₂ that transfer electrons from the valence band of TiO₂ to the conduction band through electron-hole pair formation. The conduction band surface electron is consumed by reaction with O₂ and simultaneously the holes in the valence band react with OH or H₂O species in turn gives the hydroxyl radical. This hydroxyl radical destroys the available organic chemical contaminants

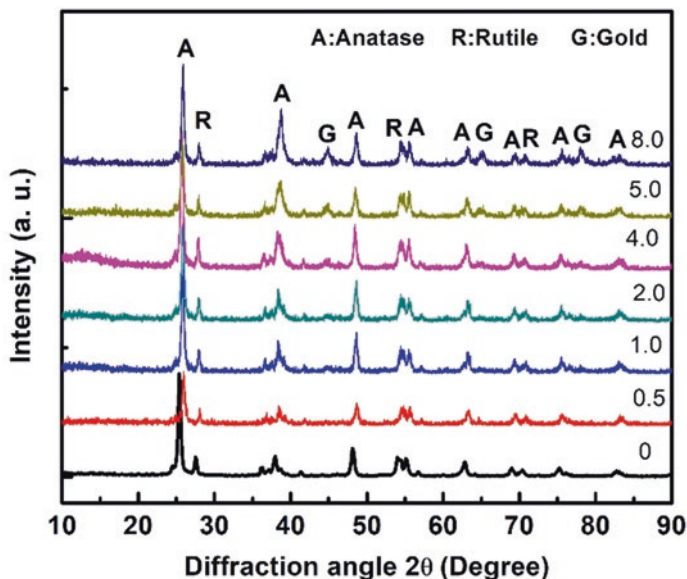


Fig. 14.2 X-ray diffraction patterns of rGO-TiO₂ with different Au wt%

in air, water, and soil through photo-catalytic oxidation. Further, this technological process is also used for the treatment of polluted surface and groundwater, waste water, and drinking water.

MoS₂/CuO heterostructural nanoflowers (Li et al. 2015a, b) and MoS₂/VO₂ hybrids (Chen et al. 2018) were developed by using two-step hydrothermal process, which significantly enhanced the photo-catalytic activity as compared to only MoS₂ nanoflower. Recently, bimetallic Co-Mn oxides/carbon hybrid based on CoMn₂O₄ anchored onto reduced graphene oxide and N-doped reduced graphene oxide via a hydrothermal method for the application in Zn-air batteries. Both catalysts displayed ORR half-wave potential of 110 and 60 mV lower than that of the state of art Pt/C catalyst, respectively (Gebremariam et al. 2018).

14.5.3 Carbon Nanomaterials

Presently, the development of carbon polymorphs such as graphite, diamond, amorphous carbon or diamond-like carbon, fullerenes, and carbon nanotubes has considered as a vital ingredients of the technological materials. But the phase stabilities of these polymorphs and their physico-chemical phenomena for the formation is still unknown. Hence, a large number of efforts were put to synthesize them with varied condition. Therefore, it is observed that the stabilities of graphite and diamond were mainly controlled by pressure-temperature tuning in the system

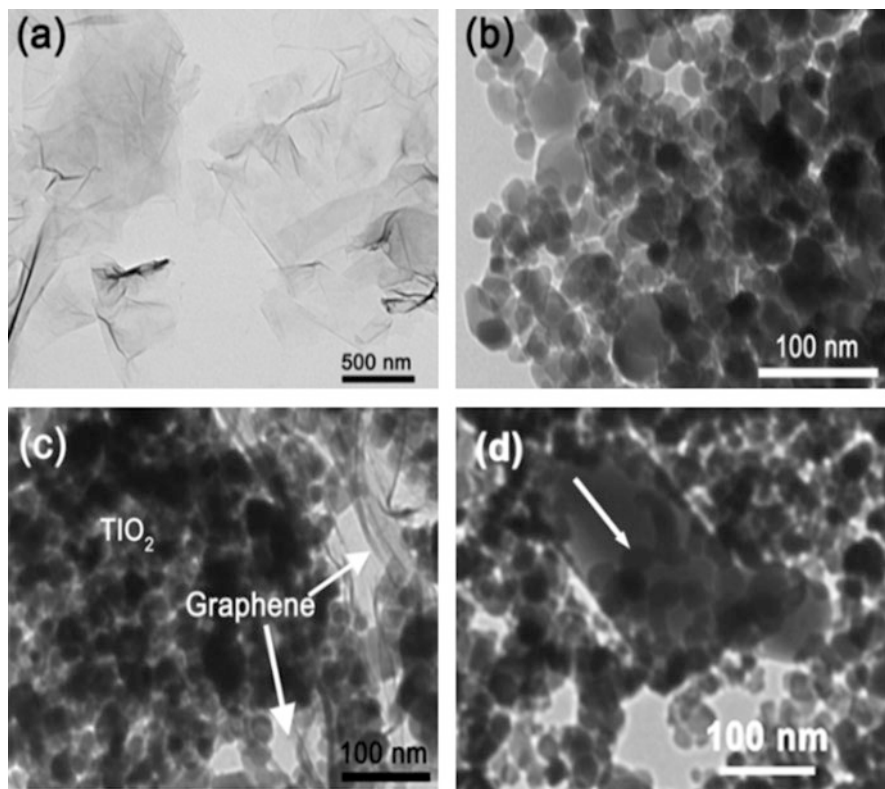


Fig. 14.3 TEM micrographs of (a) graphene oxide, (b) TiO₂, (c) rGO-TiO₂, and (d) Au-rGO-TiO₂

(Melto et al. 1974; Navon 1991; Heggerty 1986). The hydrothermal (Vasilev et al. 1968; Orlov 1973) process provoked the material researchers to explore the possibility of synthesizing them at fairly low pressure and temperature conditions. Because it is highly promising for reactions involving volatiles, as they attain the supercritical fluid state and supercritical fluids are known for their greater ability to dissolve non-volatile solids (Orlov 1973). The formation of various carbon polymorphs was reported by Gogotsi et al. (1995, 1996) and Roy et al. (1996) in hydrothermal conditions by decomposition of silicon carbide in supercritical water.

Further, Basavalingu et al. (2001a, b) have explored the possibilities of producing carbon polymorphs under hydrothermal conditions through decomposition of silicon carbide in the presence of organic compounds instead of pure water at above 700 °C and 100 MPa. Here, the decomposition of the silicon carbide occurs either to quartz or to cristobalite with high yield carbon particles. The shape of the carbon particles formed in this process are discrete or linked spherical having elongated and irregular with pore diameter of 20–30 nm. Further, according to Schmidt and Benndorf (1998), dissociation of organic molecules in presence of higher

concentration of atomic hydrogen and C_1H_x radicals is assumed an ideal environment for sp^3 -carbon phase stabilization in stimulated natural environments. It is also found that this stabilizer not only increased the yield of the carbon particles but also allows the control over the tailoring of the shape of the particles. Later on, the growth of the of diamond/ sp^3 hybridized carbon were also successfully done without using diamond precursor seed or the metal catalysts in hydrothermal conditions (Basavalingu et al. 2006, 2007).

14.5.4 Carbon Nanotubes

The development of the materials in tube structure in nano-dimension was the beginning of the new era of the materials science for the technology point of view. Materials designed in the nanotube structure are carbon nanotubes (CNTs), barium titanate (BTNT), strontium titanate nanotubes (STNTs), titania nanotube (TNT), silicon nanotube (SNT), antimony nanotubes (SbNTs), and gallium nitride nanotube (GNT) were developed (Ijima 1991; Seo et al. 2001; Wang et al. 2003; Goldberger et al. 2003; Tsai and Teng 2004; Zhao et al. 2005; Qui et al. 2005). Among these materials, the CNTs got huge popularity within the scientific and technological research due to outstanding electrical, optical, catalytic, and mechanical properties. It is considered as the potential materials for designing MEMS and NEMS devices. The benefits of the use of CNTs for such applications are due to ease of alignment in different orientation as per the need of the devices such as field effect transistors, electron-field emitters, and many more (Singh et al. 2014; Katayama et al. 1998). The CNTs exist in two different structure, namely single wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs). The structure of the carbon networks such as carbon-carbon single and double bonds available in CNTs and their conjugated structure not only provides the essence of the polymeric but also the retaining some analogous optoelectronic characteristics of other conjugated polymers. Because of owing the conjugated polymer nature, it is also considered as quantum wires (Yakobson and Smalley 1997; Ajayan and Ebbesen 1997). Further, the unusual coupling of the molecular symmetries, the CNTs became very attractive for many other potential applications such as single molecular transistors, scanning probe microscope tips, electrochemical energy storage, photo-catalyst, protein/DNA supports, filtration membranes, and artificial muscles (Frank et al. 1998; Dai et al. 1996; Che et al. 1998; Guo et al. 1998).

Therefore, the selection of the methods for the synthesis of the CNTs is an important task. The commonly known process for synthesis of the CNTs is the CVD method and pyrolysis of hydrocarbons. Both processes require metal as a catalyst. The yield is very low in this process. The observation of appearance of the natural MWCNTs with rocks of hydrothermal origin (DeVries et al. 1994) drawn possibility that the hydrothermal process may be a reproducible fabrication method of it. Gogotsi and his group (1995) developed hydrothermal CNTs using a polyethylene (PE) or ethylene glycol (EG) and water with Ni powder in a sealed gold capsule at

high pressure and temperature. They found that CNTs can be synthesized by using any liquid, solid, or gaseous carbon source. Basavalingu et al. 2006 have further studied the transformation of SWCNTs to MWCNTs under hydrothermal conditions using SWCNTs in the Tuttle-type autoclaves filled with double distilled water as a solvent with varying temperature from 200 to 800 °C at a pressure of 100 MPa for 30 min to 48 h. Initially, the SWCNTs slowly transformed into polyhedral graphitic nanoparticles above 550 °C and, then finally into MWCNTs after 800 °C and 48 h of treatment. Thereafter, several groups (Motiei et al. 2001; Lee et al. 2004; Chang et al. 2002) have synthesized the CNTs using different types of carbon-based precursor materials such as CO₂ and supercritical toluene and appropriate catalyst like Mg, Fe, or FePt nanocrystals, under hydrothermal techniques. The hydrothermal technique may offer special advantages for the processing of materials in terms of high quality with control over the tube diameter and structures.

14.6 Applications for Renewal Energy Harvesting

Energy crisis is the worldwide main concern since fossil fuels are facing rapid depletion and its consumption contributes to the rise in the average global temperature. Among the challenges to be embedded lately with agricultural activities is to explore clean and renewable energy resources.

14.6.1 *Photo-Catalytic Hydrogen Evolution from Water Splitting*

Considering an ideal fuel for the future, hydrogen can be produced from clean and renewable energy sources like water. First time, the photo-electrochemical hydrogen production was reported by Fujishima and Honda (1972) and after that many reports were published on the semiconductor photo-catalysis (Asahi et al. 2001; Khaselev and Turner 1998; Zou et al. 2001; Fox and Dulay 1993). Mostly emphasize the semiconductor photo-catalytic water and environmental purification (Hoffmann et al. 1995; Herrmann 1999), but very few of them are related to photo-catalytic hydrogen production (Hoffmann et al. 1995; Herrmann 1999; Wu et al. 2016; Zhu et al. 2018). Table 14.3 presents the photo-catalytic semiconductor materials used for the hydrogen production from water.

Recently, Singh et al. (2014) prepared reduced graphene oxide (rGO)-TiO₂ nanocomposite hydrothermally and its photo-catalytic properties for H₂ evolution values were demonstrated in Fig. 14.4. The H₂ values were recorded after irradiation of solar spectrum in UV-Visible region in presence of methanol as a scavenger. The TiO₂ samples produce very low H₂, i.e., 0.56 mmol (i.e., 112 μmol h⁻¹), whereas

Table 14.3 Recent photo-catalysts for water splitting H₂ production

S. no.	Photo-catalysts	H ₂ -evolution ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	References
1.	Pt, Cr, Ta loaded TiO ₂	11.7	Tanigawa and Irie (2016)
2.	Cu/Ga/In/S/TiO ₂	50.6	Kandiel and Takanabe (2016)
3.	1 wt% Pt/C-HS-TiO ₂	5713.6	Zhu et al. (2016)
4.	Platinized sub-10 nm rutile TiO ₂ (1 wt% Pt)	932	Li et al. (2015)
5.	Rh- and La-Co doped SrTiO ₃	84	Wang et al. (2014)
6.	Cu _{1.945} -Zn ₁ Cd ₁ (0 ≤ x ≤ 1)	7735	Chen et al. (2016)
7.	MoS ₂ /Co ₂ O ₃ /poly(heptazine imide)	0.67	Dontsova et al. (2015)
8.	Bi ₄ NbO ₈ Cl	6.25	Fujito et al. (2016)
9.	CdS nanorod/ZnS nanoparticle	239	Jiang et al. (2016)
10.	Ni/CdS/g-C ₃ N ₄	1258.7	Yue et al. (2016)
11.	CdS/WS/graphene	1842	Xiang et al. (2016)
12.	V-doped TiO ₂ /RGO	160	Agegehu et al. (2016)
13.	Pt/g-C ₃ N ₄ conjugated polymers	1.2	Zhang et al. (2016)
14.	Au-TiO ₂ C ₃ N ₄ Nanohybrids	647	Zhang et al. (2016)
15.	SrTiO ₃ :La,Rh/Au/BiVO ₄ :Mo	90	Wang et al. (2016)
16.	CoOx-B/TiO ₂ -TaON	40	Gujral et al. (2016)
17.	MoS ₂ /CuInS ₂	202	Yuan et al. (2016)
18.	Copper-organic framework; H ₂ PtCl ₆	30	Wu et al. (2016)
19.	BP/BiVO ₄	160	Zhu et al. (2018)
20.	Bi ₄ TaO ₈ X (X = Cl, Br)	0.15	Tao et al. (2017)
21.	ZnIn ₂ S ₄ /In(OH) ₃	1030.1	Zhao et al. (2018)

these values are dramatically enhanced after the addition of rGO with TiO₂. Small amount of rGO, i.e., 0.5 wt% produces 1.1 mole of H₂ which is about 1.8-fold more than the TiO₂. A maximum of 1.34 mmol H₂ (i.e., 268 $\mu\text{mol h}^{-1}$), i.e., 2.4-fold was obtained in case of rGO amount of 1.0 wt% mixed with TiO₂. The enhancement in the H₂ evolution in presence of rGO is due to excellent electron accepting and transferring capability, and the capacity to restrain the recombination of electrons-holes effectively due to two-dimensional π -conjugation structure of graphene (Zhang et al. 2010; Yu et al. 2009). More than 1.0 wt% rGO reduces the photo-catalytic activity results reduction in H₂ production value.

Further, the Au was loaded on the rGO-TiO₂ nanocomposites to see the plasmonic effect on the H₂ evolution. Figure 14.5 shows the photo-catalytic activity of the Au co-catalyst loaded on 1 wt% rGO-TiO₂. The 0.5 wt% Au loading shows the H₂ evolution value of 7 mmol (i.e., 1.4 mmol h⁻¹) which is 5.2-fold higher than 1 wt% rGO-TiO₂. The maximum value of H₂ production was achieved 12 mmol (i.e., 2.4 mmol h⁻¹) in case of 2.0 wt% Au loading. More than 2.0 wt% Au contents loading gradually decreases the H₂ evolution activity.

The charge transfer mechanism is projected in Fig. 14.6 and the photo-catalysts reaction steps involved in water splitting H₂ evolution are summarized as follows:

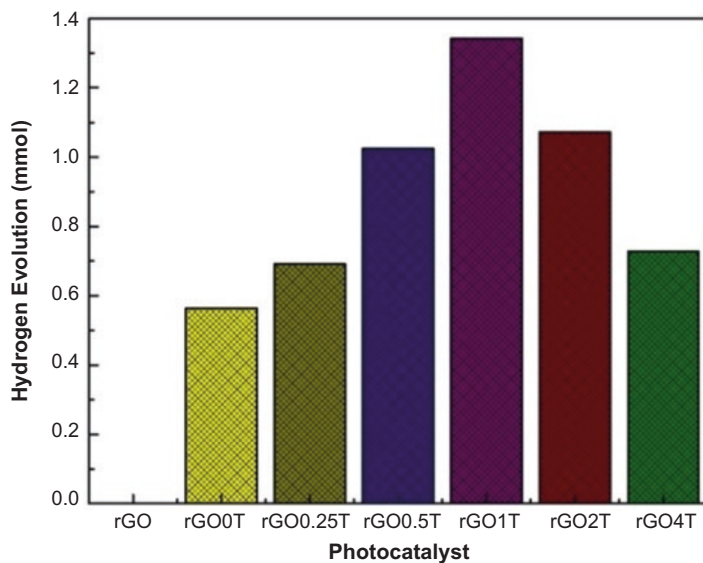


Fig. 14.4 Photo-catalytic activity of photo-catalyst for H_2 evolution from methanol aqueous solution under UV-Visible light irradiation (Singh et al. 2014)

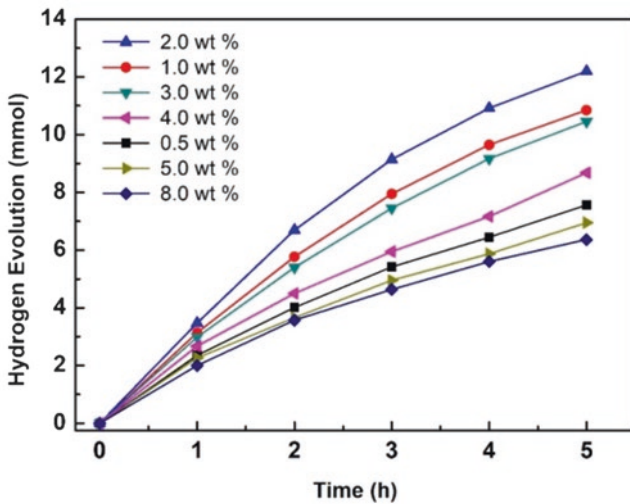


Fig. 14.5 Hydrogen evolution through plasmonic active Au loaded rGO1T photo-catalysts from methanol aqueous solution under UV-visible light (Singh et al. 2014)

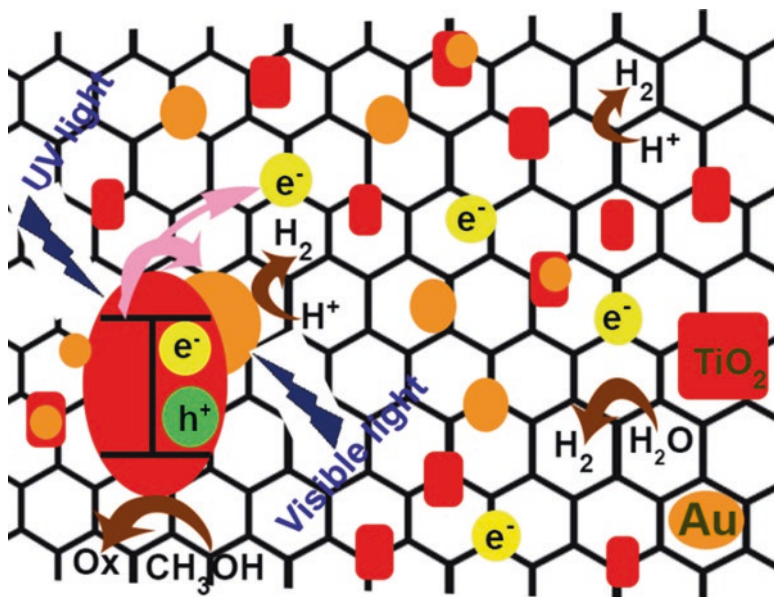
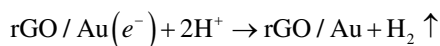
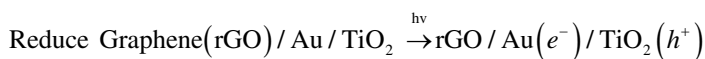


Fig. 14.6 Charge transfer process in Au/graphene/TiO₂ photo-catalyst (Singh et al. 2014)



14.6.2 Dye-Sensitized Solar Cells (DSSC)

Photovoltaic (PV) technology is also considered as one of the feasible green resources for electrical energy generation via solar technology. In this regard, the dye-sensitized solar cell (DSSC) is of countless importance due to several attractive features such as designing and fabrication of DSSC is inexpensive, flexible, transparent, and sensitive to low light levels. Besides its easiness to be used in larger applications, the production of the materials used for making DSSC an ideal candidate needs to explore the techniques which are able to increase the materials efficiency of solar to energy conversion. The hydrothermal techniques is also considered as one of the viable means for the production of materials in comparison to other available methods.

Wang et al. (2009) were directly grown large-scale macroporous TiO_2 nanowires on spiral-shaped titanium wires as photoanodes of dye-sensitized solar cells (DSSCs) via a facile hydrothermal reaction without any seeds, templates, and TiO_2 powder. The efficiency of 0.86% for the DSSC was obtained with a J_{sc} of 2.30 mA/cm², V_{oc} of 616 mV, and FF of 0.61. This MNT-based mini DSSC is a promising photovoltaic device for applications in the fields of high-integrated microelectronic equipment. Zn_2SnO_4 (ZTO) nanoparticles developed by employing same process were used as a DSSC with commercial photo sensitizers such as N719 and N3 dye molecules (Das et al. 2016; 2018a, b). The N3 dye molecules give better dye sensitization property than N719 dye molecules. The solar devices designed with ZTO-N719 showed improved photovoltaic performance compared to the ZTO-N3 devices. The overall conversion efficiency of 2.56% is achieved under 1 SUN 1.5 AM illumination and sensitization for 12 h. Rajamanickam et al. (2017) implemented the hydrothermally TiO_2 nanorods prepared at low temperature for solar cell as a photoanode materials and found the power conversion efficiency of 5.42% along with the open-circuit voltage, short-circuit current density and fill factor of 0.647 V, 13.64 mA/cm², and 61.5%, respectively. After the use of 2500 h runs of it in a solar cell, J - V characteristics were remaining constant.

Further, the perovskite-based solar cell were designed by Dunlap-Shohl et al. (2018) using delafossite oxides (CuCrO_2 , i.e., CCO) as promising hole transport layer because of wide band gap and favorable energy band alignment relative to the perovskite absorber. Pure Phase CCO films were deposited by spin casting suspensions of hydrothermally synthesized CCO nanoparticles in the form of glass/ITO/CCO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /C60/BCP/Ag as solar cell device structure. It exhibits highly stable power conversion efficiencies exceeding 14%.

14.7 Future Scope of Hydrothermal Synthesis Process

The futuristic scope of hydrothermal synthesis process for advanced technological application depends upon its operation simplicity with nanometer resolution, control over the reaction kinetics, suitability with the theoretical approaches to the growth of materials from solutions, development of in situ mapping of techniques, in situ surface modification and attaining high dispersion of materials. It offers many advantages over conventional and non-conventional synthetic methods. All forms such as powders, fibers, films of metal, ceramics, and polymers can be synthesized by hydrothermal synthesis. Present continuous demands of this technology lead it not only within the materials growth but also it explores towards the various branches of science and technology. For instance, the hydrothermal technique is regarded as the most appropriate technique to formulate the materials for advanced technology like solar energy conversion, hydrogen generation from water, drug delivery, hyperthermia, neutron therapy, bio-imaging, fluorescent labeling, and more. The beauty of this method is to ease the control of the size and shape of the nanocrystals, and significantly reduced aggregation levels which is not possible in

other processing techniques. As continuous increasing demand for composite nanostructures, it also offers a unique method for designing polymer-ceramic composites or textured ceramic-ceramic composites with anisotropic properties.

14.8 Conclusion

Hydrothermal technology for the processing of advanced materials has gained lots of advantages due to easy adaptability and being environmental friendly. The great advantages of hydrothermal technology for nanomaterials processing are the production of particles that are mono-dispersed with total control over their shape and size in addition to their chemical homogeneity with the highest dispersibility. A great variety of advanced nanomaterials whether nanoparticles, or nanocomposites covering metals, metal oxides, semiconductors including II–VI and III–V compounds, silicates, sulfides, hydroxides, tungstates, titanates, carbon, zeolites ceramics, composites, etc. have been processed using hydrothermal technology. The use of multi-energy systems like microwave-hydrothermal, electro-chemical-hydrothermal, or mechano-chemical-hydrothermal drives this technology to a new and totally unexplored avenue in present scenario. The use of capping agents, surfactants, and other organic molecules contribute greatly to the surface modification of these nanocrystals to obtain the desired physico-chemical characteristics. Hydrothermal technology has the ability to significantly accelerate the kinetics of synthesis, to model the theoretical approaches from solutions, and to develop in situ observation techniques. The combination of hydrothermal technology and nanotechnology can answer most of the problems associated with advanced materials processing.

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Chapter 15

Biomedical Applications and Characteristics of Graphene Nanoparticles and Graphene-Based Nanocomposites



S. Rajeshkumar and P. Veena

15.1 Introduction

Graphene is the nanomaterial consisting of a single layer of carbon arranged in an allotropic form. Graphene is chemically, mechanically, and thermally stable compound (Wang et al. 2017a). It has various other properties such as large specific surface area and high flexibility (Hsieh et al. 2015). Graphene oxide, reduced graphene oxide, graphene nanosheets, graphene nanocrystals, graphene nanocubes, graphene nanotubes, graphene quantum dots, and others are also widely studied due to its exceptional properties (Fig. 15.1). Different methods are carried out to prepare graphene such as chemical vapor deposition, chemical or electrochemical reduction, and mechanical exfoliation (Kim et al. 2017). The graphene layer is formed by chemical vapor deposition. Graphene oxide (GO) is prepared by oxidation of purified graphite by Hummer's method and reduced graphene oxide (rGO) is prepared by chemical reduction of reduced graphene oxide (Devi and Kumar 2018).

Graphene is stronger than many other metals and it is highly flexible. It is the strongest material than any other material known. Graphene has many such notable features that allow the inorganic nanoparticle to accumulate in it to form nanocomposites (Wei et al. 2017). Graphene nanoparticles are decorated with other nanoparticles on its surface for more beneficial property (Luan et al. 2018). Graphene is mixed with several other nanoparticles such as metals (Ag, Au, Cu, Zn), non-metals (chitosan, polymers, epoxy), or metal oxides (TiO_2 , ZnO) in order to produce nanocomposites (Acar Bozkurt 2017) (Fig. 15.2).

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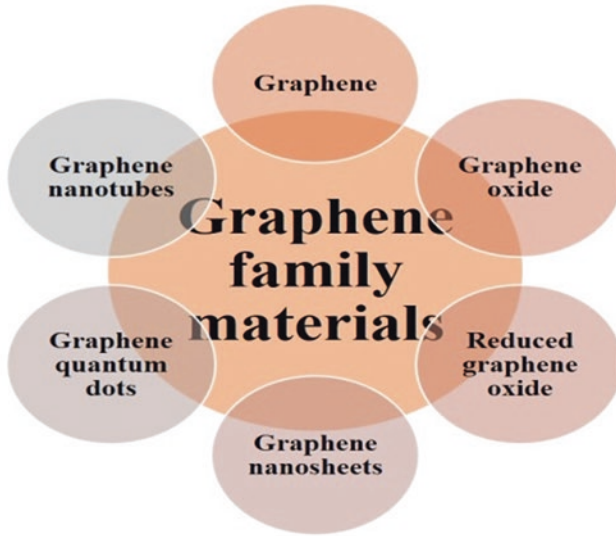


Fig. 15.1 Graphene materials

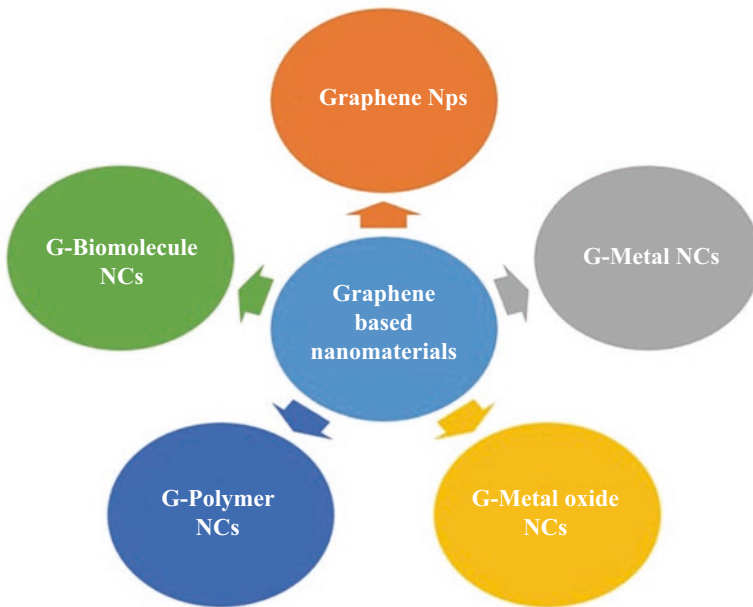


Fig. 15.2 Graphene-based nanocomposites

Graphene nanocomposites have tremendous application in various fields such as antimicrobial, anticancer, biosensing, bioimaging, and drug delivery (Khalil et al. 2017) (Fig. 15.3).

In this review article, we focused and discussed the major application of graphene nanoparticles and graphene-based nanocomposites such as graphene-gold, graphene-silver, graphene-zinc, and graphene-nickel in various biomedical aspects such as a biosensor, bioimaging, antimicrobial, anticancer drug delivery, etc. (Fig. 15.4).

15.2 Application of Graphene Nanoparticles and Graphene-Based Nanocomposites

15.2.1 Graphene Nanoparticles

Graphene nanoparticles (GNPs) have gained noticeable attention in the biomedical field such as tissue engineering, bone regeneration, bio-conductivity, drug delivery, etc. Low oxygen graphene nanoparticles have an exceptional property of osteoinduction and osteoconduction which helps in the bone regeneration of mesenchymal stem cells. They are used to treat trauma in the bone tissue and retaining the stem cell activity (Elkhenany et al. 2017). Graphene has a 2D and unique structure

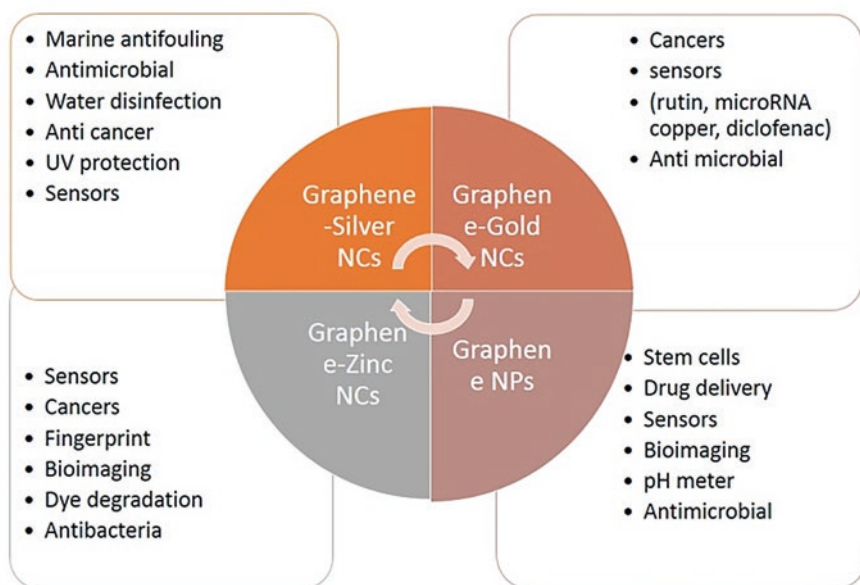


Fig. 15.3 Graphene NPs and graphene-based NCs applications

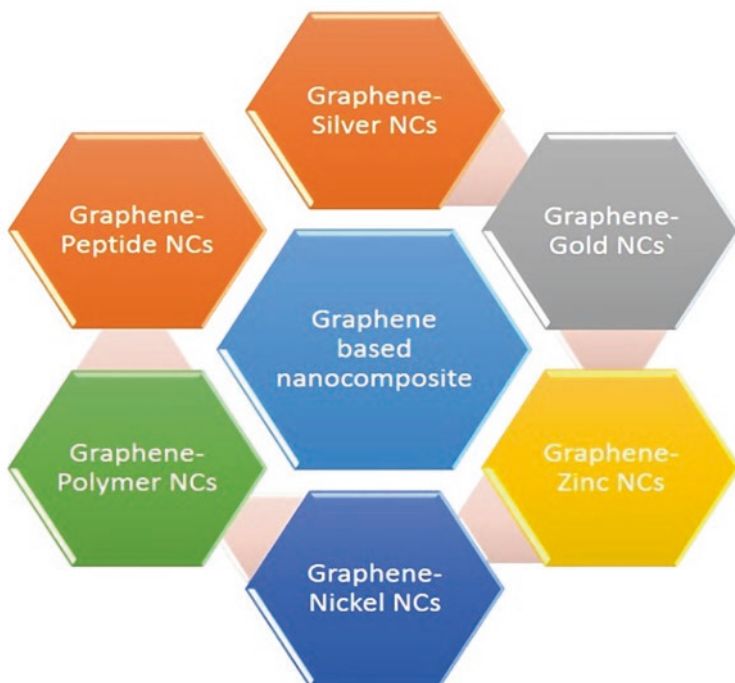


Fig. 15.4 Widely used graphene-based nanocomposite

containing various special properties such as high specific area, modified easily and it is a strong material. This property allows the graphene to act as a carrier for a multifunctional drug delivery (Zhao et al. 2017b). A single layer graphene intensifies the property of the sensors. Graphene is used widely in sensors and biosensors such as enzymatic and non-enzymatic glucose sensors, hydrogen peroxide sensors, and immuno-sensors (Bollella et al. 2017). Nanographene oxide has a photoluminescence property which is utilized for bioimaging technique such as fluorescent imaging and 2 photon fluorescent imaging (Lin et al. 2016). Remarkable properties of the graphene such as larger surface area provide the pH meter a higher sensitivity and flexibility compared to a glass electrode. Optical graphene oxide has an insulating property which is usually involved in optical sensors (Salvo et al. 2018). An antimicrobial property of the graphene oxide is attained by the sharp edges of the GO (graphene oxide) which causes damages to the cell membrane of the bacteria that decreases the drug resistivity (Yousefi et al. 2017) (Table 15.1).

Table 15.1 Biomedical application of graphene nanoparticles

S. no.	Application	Function	Characteristics	Reference
1	Stem cell	Osteoinductive and osteoconductive platform for stem cell and bone regeneration	Graphene thickness is 1.0–1.2 nm	Elkhenany et al. (2017)
2	Drug delivery	The unique structure of graphene acts as a carrier for multifunctional drug delivery	Graphene nanoparticles size is 5 nm	Zhao et al. (2017a, b)
3	Sensors	Sensors and biosensors are made effective using graphene, GO, and rGO	500 nm of nanoflakes size and 1 nm of the thickness of graphene	Bollella et al. (2017)
4	Bioimaging	Graphene used in fluorescent imaging and 2 photon fluorescent imaging	Graphene nanoparticles size of 10–60 nm	Lin et al. (2016)
5	pH meter	Fabrication of pH meter with graphene increases its sensitivity and quality	3–20 nm usually between 100 nm of graphene quantum dots	Salvo et al. (2018)
6	Antimicrobial	Exceptional properties of graphene oxide contain high antimicrobial property and control drug-resistant microbes	100 nm, 200 nm, and 50 nm of graphene is used for different effect on bacteria	Yousefi et al. (2017)

15.2.2 Graphene-Based Nanocomposites

15.2.2.1 Graphene-Gold Nanocomposites

Gold is an excellent thermal and electrical conductor. This property helps these nanocomposites in electrochemical sensing. Graphene and gold nanoparticles are coated on an acupuncture needle for sensing rutin. Acupuncture needle has a small surface area which acts as an electrode for sensing the lower quantity of sample (Niu et al. 2018). Another sensor for detecting rutin is made of carbon screen-printed electrode which is coated with the graphene, gold NPs, and chitosan (Apetrei and Apetrei 2018). Graphene and gold nanoparticles are used for fabricating the PEC aptasensor (photo-electrochemical aptasensor) which is used to sense the diclofenac, an anti-inflammatory drug (Okoth et al. 2018). Reduced graphene oxide (rGO) and gold nanoparticles are used for fabricating the electrode for detection of copper in high salt electrolyte substrate. Reduced graphene oxide has a large surface area which has many active sites and electrical transfer is promoted by gold. Nafion is a polymer that is used as cation exchanger to bind the reduced graphene oxide and gold together tightly. Five to 10 nm diameter of silver nanoparticles is used to decorate the graphene on the electrode surface (Liu et al. 2017). SPR biosensor (sensitive surface plasmon resonance) has two different layers, the bottom layer made of graphene oxide to attain maximum surface area for microRNA to get adhere onto the surface and the top layer made of gold for providing signal amplification. The detection limit of microRNA is measured as 0.1 fM (Li et al. 2017). Graphene-based

sensor plays a vital role in cancer detection. Graphene oxide and gold nanoparticles are fabricated on a glass electrode for detecting the cancer biomarkers. Graphene oxide helps to detect the cancer biomarkers and gold nanoparticles provide the signaling (Ali et al. 2017). Graphene and graphene-based nanocomposites possess a promising application in cancer disease. Graphene-gold based nanocomposite with its exceptional properties it acts as therapeutic tools and detection of cancer disease. Graphene-silver nanocomposite acts as various sensors such as gene biosensor, immune-sensor, and enzyme biosensor. Various therapeutic techniques also involve G-Au NPs such as phototherapy, combination therapy, and chemotherapeutic drug delivery (Al-ani et al. 2017) (Table 15.2).

15.2.2.2 Graphene-Silver Based Nanocomposites

An excellent antimicrobial property of silver is utilized and widely used in several applications. The reduced graphene oxide which is ornamented with the silver nanoparticles shows higher antibacterial activity by showing the enhanced zone of inhibition. The large surface area of the graphene promotes the activity of the “attacking and killing” mechanism (Ganguly et al. 2017). Graphene decorated with reduced silver is used as a sensor to detect the hydrogen sulfide gas. Doped graphene allows fabricating the sensor to achieve high resistance and more sensitivity to hydrogen sulfide gas (Ovsianytzkyi et al. 2018). Composite G/Ag NPs also

Table 15.2 Biomedical application of graphene-gold nanocomposite

S. no.	Application	Function	Characterization	Reference
1	Cancer	Early detection of breast cancer biomarkers using graphene oxide-gold coated electrodes with detection limit 0.16 and 0.23 nM	The thickness of graphene sheet is 0.34 nm and gold nanoparticles size is 10–50 nm	Ali et al. (2017)
		Graphene-Au nanoparticle sensors for detecting and tools for therapy	Gold nanoparticles are determined to be having a particle size of 100 nm	Al-Ani et al. (2017)
2	Sensors	Detection of rutin with detection limit 1.1×10^{-8} M	Nanoflakes structure of graphene decorated with gold on its surface	Niu et al. (2018) and Apetrei and Apetrei (2018)
		Detection of diclofenac		Okoth et al. (2018)
		Detection of copper from seawater	Gold nanoparticles diameter is about 5–10 nm and thickness of graphene is 0.8–1.2 nm	Liu et al. (2017)
		Detection of microRNA	The average size of gold nanoparticles is 16 nm to 22 nm.	Li et al. (2017)

applied as water disinfectant due to its elasticity and large porosity. Graphene nanoparticles and silver nanoparticles are ornamented with the melamine sponge which is then submerged in a suspension of bacteria. The bacterial membrane is destructed by the composite providing antibacterial property to the sponge (Deng et al. 2017). Graphene/silver nanocomposites are coated with a polyester fabric to enhance the quality such as UV and mechanical protection. Fabric coated with graphene/silver nanocomposites is also highly durable, stretchable, foldable, and flexible (Ouadil et al. 2017). Reduced graphene oxide-silver nanoparticles are synthesized by the green method and reduced using vitamin C to the composite. The cytotoxicity study of the synthesized nanocomposites towards human lung cancer is significantly high compared to silver nanoparticles and graphene oxide. The cytotoxicity of the rGO-Ag NPs is IC₅₀ of 30 $\mu\text{g}/\text{mL}$ (Kavinkumar et al. 2017). Methimazole can be detected sensitively by the electrode that is fabricated by the graphene and the silver NPs. Graphene nanosheets are synthesized by Hummer's method from graphite. The surface of the graphene is decorated with the Ag NPs. The composite is fabricated on the carbon paste electrode. Due to the large surface area which leads to higher active sites the adsorption of the methimazole is high and sensitive than the carbon paste electrode (Alaqad et al. 2017). Antimicrobial property of silver assists in the process of antifouling of the submerged surfaced undersea. Graphene material decorated with silver nanoparticles is fabricated on the submerged surfaces. The antibacterial property of the silver and structure of graphene together act as an antifouling agent. The diameter of the silver nanoparticle is 2–5 nm (Yee et al. 2016) (Table 15.3).

15.2.2.3 Graphene-Zinc Based Nanocomposite

Chemically converted graphene decorated with Au and ZnO is synthesized in-situ by one-pot low temperature. Size of the Zn nanoparticles is 30–60 nm and Au particles are –11.3 nm. AZG (Au-ZnO-Graphene) nanocomposite is immobilized with BSA (bovine serum albumin) which has high biocompatibility and shows maximum cell viability for human ovarian cancer cells (Naskar et al. 2018). Graphene nanoparticles with zinc are used to sense hydrogen gas at 200 ppm. Graphene-zinc oxide nanocomposite increases the sensitivity and decreases the minimum operable temperature. The prepared composite powder is covered on the alumina substrate for gas sensing. The XRD reveals that the graphene-zinc formed a crystalline structure and the FTIR value is 1564 cm^{-1} (Anand et al. 2014). Highly sensitive DNA biosensor made using graphene and zinc oxide is effective in detecting the H5 gene of Avian Influenza. The sensitivity of geno sensor is increased to ($P < 0.05$). The sensitivity of this biosensor is $3.2580\text{ m AmM } \text{\AA}^{-1}$ and the detection limit is 7.4357 mM (Low et al. 2016). RNA sequence can also be detected effectively using biosensors fabricated with the zinc-graphene nanocomposite because of its high specific area and good biocompatibility. A single-strandard DNA sequence is synthesized using coconut cadang cadang viroid (CCCVd) complementary RNA sequence. The synthesized sequence is immobilized on the surface of the biosensor

Table 15.3 Biomedical application of graphene-silver nanocomposite

S. no.	Application	Function	Characteristic	Reference
1	Antibacterial	“Capturing and killing” mechanism carried out by silver nanoparticles to kill <i>E.coli</i> with inhibition zone 2.1 cm	Crystal structure with 0.44 nm interspace in reduced graphene oxide and silver nanocomposites	Ganguly et al. (2017)
2	Sensor	Hydrogen sulfide gas sensor electrode	Noncrystalline smooth structure with a 10–30 nm particles size of silver nanoparticles	Ovsianytzkyi et al. (2018)
		Detection of doxorubicin with the detection limit of 2 nM	XRD shows dendritic structure and the nanoparticles distributed on the surface of the reduced GO	Guo et al. (2017)
		Methimazole detection	Silver particle size is 8–12 nm	Alaqad et al. (2017)
		Methylene blue detection	Silver-reduced graphene oxide is quasi-spherical in shape and the diameter is 28–32 nm	Chettri et al. (2017)
3	Water disinfection	Preparation of melamine sponge with graphene-silver NPs	Silver nanoparticles distributed on the MS is 38.41 ± 13.83 nm	Deng et al. (2017)
4	Anticancer activity	Higher cytotoxicity level of rGO-gold nanoparticles towards lung cancer cell	Size of the silver nanoparticles is greater than 5 nm	Kavinkumar et al. (2017)
6	UV protection fabrics	Ag-G NPs are coated on a fabric for UV protection	Graphene oxide has to interspace between 0.9 nm	Ouadil et al. (2017)
6	Marine antifouling agent	Antimicrobial property of silver acts against the bacterial growth on submerged surfaces	Silver nanoparticles have a size of 76–82 nm	Yee et al. (2016)

fabricated with GZO nanocomposite which provides good detection limit and sensitivity. The detection limit is 4.3×10^{-12} M. The zinc oxide and graphene nanocomposites are formed into a clear crystalline structure. Detection of ammonia is achieved successfully at room temperature using zinc oxide nanowire and reduced graphene oxide. Zinc transfers the electron to the graphene which increases the sensitivity to the sensor more than bare graphene sensor (Wang et al. 2017b). Bioimaging can be successfully obtained by using AgInZnS and graphene oxide nanocomposite. Mice organs and cancer cells are effectively imaged using this nanocomposite. The absence of toxic cadmium reduces the cytotoxicity of the cells. The synthesized nanocomposites emit four colors red, yellow, green, and orange. The nanocomposites prepared shows highly crystalline structure with the diameter of 4–5 nm. This is effectively applied in bioimaging of breast cancer cells

SK-BR-3 (Zang et al. 2017). A study discovered a new drug carrier made of zinc-clinoptilolite/graphene which has high drug load capacity and possesses a property to release the drug slowly into the cell medium. The research is successfully carried out with a cancer drug—doxorubicin (Khatamian et al. 2016). Zinc oxide is decorated with the graphene oxide nanoparticles. The size of the zinc oxide is 20–25 nm with a spherical shape. The synthesized nanocomposite is used for photodegrading the dyes such as methyl red, congo red, crystal violet, and neutral red. The ZnO-GO nanocomposite effectively photodegrades azo dye and bare ZnO nanoparticles (Atchudan et al. 2017) (Table 15.4).

Table 15.4 Graphene-zinc based nanocomposite

S. no.	Application	Function	Characteristics	Reference
1	Latent Fingerprint detection	TiO ₂ , iron oxide, and ZnO are used as developing fingerprint powders		Amrutha et al. (2017)
2	Cancer	Gold-zinc-graphene immobilized with BSA (bovine serum albumin) has maximum CV in human ovarian cancer cells	The average particle size of zinc oxide is 11.30 nm and gold is 30–60 nm	Naskar et al. (2018)
3	Sensors	Hydrogen gas detection by ZnO and graphene	Flower-like structure distributed on the graphene sheet	Anand et al. (2014)
		Avian Influenza H5 gene detection by DNA biosensor made of graphene-ZnO	Spherical in shape and the average particle size is 200 nm	Low et al. (2016)
		Single-stranded RNA detection genosensor—CCCVd sequence	Zinc oxide is observed to be Qazi spherical shape	Low et al. (2017)
		Glucose sensor using nickel and zinc is effective in detecting glucose from human serum sample	Size of nickel NPs is 18 nm and thickness of GO is 0.34 nm	Mazaheri et al. (2017)
4	Drug delivery	Zinc incorporated with graphene as a drug carrier of cancer drug—doxorubicin	XRD shows 20–30 nm thick graphene	Khatamian et al. (2016)
5	Bioimaging	Imaging of breast cancer cells SK-BR-3 using AgInZnS and graphene oxide	Average size is 10 nm	Zang et al. (2017)
6	Dye degradation	ZnO and GO nanocomposite are used effectively in the photodegradation of azodye MO, CV, CR, NR	Zinc oxide nanoparticles have 20–25 nm of diameter and spherical shape	Atchudan et al. (2017)
7	Antibacterial activity	Effective against <i>Bacillus subtilis</i> , <i>Escherichia coli</i> with 18.9 nm and 23.8 nm	XRD shows 25.9–56.2 nm of particle size	Alswat et al. (2017)

15.2.3 *Other Graphene-Based Nanocomposite*

Apart from graphene, gold, silver and zinc nanocomposite, there are several other graphene-based nanocomposites that possess effective application in various fields. Graphene and nickel nanocomposite is used in degrading radionuclides such as uranium and thorium. Uranium (VI) and thorium (IV) are adsorbed more when the temperature of the system increases. Graphene has the high surface area, pore size and density provide high absorption than another nanocomposite (Lingamdinne et al. 2017). Graphene oxide and lead possess an excellent catalytic property which is used to degrade organic dyes such as congo red, methyl orange, and methylene blue with use of reducing agent NaBH_4 (Omidvar et al. 2017). Bacterial cellulose and graphene oxide nanocomposite effectively act as a drug carrier for ibuprofen. It has high cell viability and it is effective than graphene oxide (Luo et al. 2017). When a graphene is modified with macromolecule such as peptides, DNA, and proteins in biosensors, it enhances the sensitivity and selectivity of the system. Peptide-modified graphene nanocomposite is used in many biosensors such as fluorescent biosensors, spectroscopic biosensors, electrochemical biosensors, and electronic biosensors. Among these biosensors, fluorescent biosensors and electrochemical biosensors are effective than spectroscopic biosensors and electronic biosensors. Peptide-modified graphene nanocomposite increases the biorecognition and biocompatibility of the sensors (Wang et al. 2017a). Graphene oxide modified with hydroxyapatite nanocomposite has less cytotoxicity to the human skin cancer cells (A431). The property of the nanocomposite is analyzed using BSA (bovine serum albumin). GO-HAP nanocomposite has good biocompatibility which is used in dentistry, drug delivery, and other biomedical application (Ramadas et al. 2017) (Table 15.5).

15.3 Conclusion

In summary, the graphene nanoparticles and graphene-based nanocomposites are involved in many applications in the biomedical field. Graphene is highly effective because of its exceptional properties such as high specific surface area, good physiochemical property, mechanical and electrical stability. Graphene consists of 2D structure which is used to decorate other nanoparticles such as metals, metal oxides, polymers, and biomacromolecules. Our review concludes that the graphene nanoparticles and graphene-based nanocomposite such as G-Silver NCs, G-Zinc NCs, G-Gold NCs, G-Nickel NCs, G-Polymer NCs, and G-Peptide NCs are effective in many applications such as cancer studies, antimicrobial activity, drug delivery, biosensors, marine antifouling agent, bioimaging, UV protection, and dye degradation. In future, graphene nanoparticles decorated with a suitable metal or non-metal nanoparticles can enhance the effect on graphene nanoparticles and will be useful in many biomedical fields.

Conflict of Interest The authors declared that there is no conflict of interest.

Table 15.5 Other graphene-based nanocomposite

S. no.	Nanocomposite	Application	Function	Characteristics	Reference
1	Nickel-graphene	Removing radionuclides	Nickel ferrite and reduced GO is used to remove radionuclides such as uranium and thorium from wastewater	41.41 nm size of graphene oxide and 32.16 nm of reduced graphene oxide. It is noncrystalline cube structure	Lingamdinne et al. (2017)
2	Graphene-bioglass	Bone tissue engineering	–	–	Pazarçeviren et al. (2017)
3	Graphene-lead	Dye degradation	Organic dyes such as Congo red, methyl orange, and methylene blue are degraded from water using graphene oxide and lead	11 nm particle size and spherical shape	Omidvar et al. (2017)
4	Graphene-cellulose	Drug delivery	Ibuprofen is loaded on the graphene oxide and bacterial cellulose nanocomposite for drug delivery	500 nm particle size and thick fiber porous structure	Luo et al. (2017)
5	Graphene-peptide	Biosensors	Biosensors with biomacromolecules enhance the efficiency of the sensors. It increases the selectivity and sensitivity of the sensors	Crystalline honeycomb structure of graphene with surface modified peptide	Wang et al. (2017a)
6	Graphene-hydroxyapatite	Cancer	Cytotoxicity of graphene oxide and hydroxyapatite is examined using human skin cancer cell	Diameter of Hap is –32 nm and length –60 to 85 nm	Ramadas et al. (2017)
7	Graphene oxide-PEG-folic acid	Cancer	Anticancer drug camptothecin is loaded in a graphene for its large surface area	Width of the PEG is 11.5 nm and GO is 10.5 nm	Deb and Vimala (2018)
8	Graphene-Iron-SnO ₂	Sensor	Used as humid sensor by humid air measured at room temperature	Iron nanoparticles have diameter of 17 nm	Toloman et al. (2017)
9	Graphene-nickel	Sensor	Enzymeless detection of glucose with detection limit 388.4 1A mM	Nickel particle size is 99.2 nm	Ji et al. (2017)

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Chapter 16

Nanodiagnosics Tools for Microbial Pathogenic Detection in Crop Plants



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16.1 Physiopathology of Pathogenic Infections in Plants

The annual loss of an important part of crops is, most of the time, because pest incidence. This is the reason why the nature of the mechanisms of pathogenic infection and resistance in the host is still under study at present. One of the most discussed issues is the coevolution capacity of the pathogen and the host, understood as the ability of the pathogen to infect an unknown host, and the ability of the host to defend against this new pathogen (Anderson et al. 2010).

For years, it has been investigated, without special success, if the introduction of plant species in a locality significantly reduces the infection by a certain pathogen present there. The hypothesis has been that invasive species leave behind their natural enemies, and that they do not receive special pressure from established pathogens in the areas they reach, since they are adapted to live on native species. However, the evidence on this was contradictory (Wolfe 2002; Agrawal et al. 2005; Parker and Gilbert 2007; van Kleunen and Fischer 2009) until Gilbert and Parker (2010) studied the infection of *Stemphylium solani* isolated in California on species of native and European *Trifolium*, finding a strong increase of the infection as the pathogen was confronted to the new hosts.

This evolution must occur with greater speed and amplitude in pathogens, given the speed with which they reproduce and give rise to new generations, compared with

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that of plants. Flor's theory about the existence of a gene for a gene (complementarity between the host and the pathogen) is being modified from the understanding that the interaction between them is determined by a complex set of genes in the host and the pathogen (Gilbert and Parker 2010).

Until today, a subject of deep interest in host–pathogen interactions is how plants are able to perceive the attack of pathogens. To date, two proposals are known; the first is based on Flor (1956) theory of gene-to-gene correspondence, and led to the discovery of pathogenesis-related proteins (PRPs), which are proteins produced by plants as a result of pathogen attack (Loon 1985). The PRPs are divided into two large groups, according to Tang et al. (2017):

- Cytoplasmic nucleotide binding domain leucine-rich repeat domain-containing receptors, known as NLRs (Jones et al. 2016).
- Receptors localized in cell surface, which are proteins belonging to large families of receptor-like kinases (RLKs) and receptor-like proteins (RLPs) (Jones and Dangl 2006).

The second way is based on the fact that elicitors and the molecular patterns of damage generated by microorganisms can trigger defense signals in plants, leading to the identification of the abovementioned RLKs and RLPs as recognition patterns (PRRs) of the attacks of pathogens (Boller and Felix 2009). In this way, the NLRs would be responsible for the recognition of the effects at the cytoplasm level, and the PRRs would detect the effects on the apoplast (Tang et al. 2017).

As mentioned above, the constitutive or innate immunity of the plant depends on three events: the first is that the plant can detect the attack of the pathogen; the second, that a complex system of signals is activated, and the third, the expression of defense genes (Tang et al. 2017).

Truman et al. (2013) point out that two types of processes are involved in the detection of attack, which have been called protein-triggered immunity (PTI) (Truman et al. 2013) and effector-triggered immunity (ETI) (Jones and Dangl 2006). In the first of them, pathogenic proteins are recognized by the plant through their coupling to receptors directly involved in the defense system. In the second, pathogens produce effectors that are recognized by plant proteins, unleashing defensive mechanisms.

In the PTI pathway, the recognition of the infection triggers several rapid response processes, and after a few hours the synthesis of phytohormones (ethylene, conjugates of jasmonic acid, salicylic acid) is observed, signaling for the expression of a large group of genes (Fig. 16.1).

Although the recognition of the pathogen through ETI results in a defense mediated by proteins inhibiting invasion, this occurs only in resistant or immune hosts. If the pathogen does not produce effectors capable of triggering the ETI, or if it is capable of reprogramming the transcriptome of the host thanks to other effectors, an effector-triggered susceptibility is produced (ETS) (Mengiste 2012).

Today there is abundant evidence showing that ethylene, which was originally described as “the ripening hormone,” participates in other processes of plant growth and development, and also in the response to biotic and abiotic stress (Liu et al. 2016). In Arabidopsis, a linear pathway of ethylene signaling has been discovered, leading

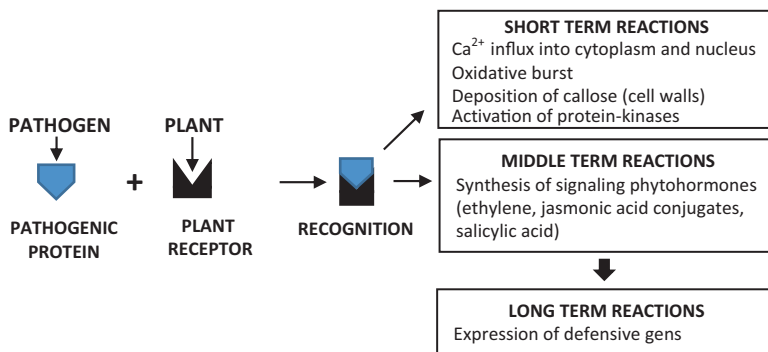


Fig. 16.1 Protein-triggered immunity (data from several authors, cited by Truman et al. 2013)

from its perception in the endoplasmic reticulum to its transcriptional regulation in the nucleus (Yang et al. 2015). However, the ethylene pathway shows diffuse patterns in terms of its participation in resistance: the ethylene insensitive mutants *ein1* and *ein2* are resistant to the biotrophic bacterium *Pseudomonas syringae* and are instead susceptible to the necrotrophic fungi *Botrytis cinerea* and *Plectosphaerella cucumerina* (van Loon et al. 2006; Chen et al. 2009).

Calmodulins are proteins containing four Ca²⁺ fixative sites. Through these bonds, they are responsible for the transport of calcium, which constitutes one of the first signs of recognition of pathogens, the subsequent production of salicylic acid, and the expression of immunity genes mediated by this phytohormone (Wang et al. 2009). Truman et al. (2013) found that three members of the CBP60 family are involved in signaling the resistance of *Arabidopsis* to *P. syringae* (one of them has a repressor effect and two have inductive effects). Apparently, these two types of actions are related to the repression of the response in the absence of the pathogen and its rapid activation when the attack begins. However, the CBP60 family is also involved in the response to abiotic stresses such as drought (Wan et al. 2012) and low temperatures (Kim et al. 2013).

It should be borne in mind that there are two large groups of pathogenic microorganisms for plants: biotrophic and necrotrophic (Glazebrook 2005). The former attack living tissues, and require them to continue alive to obtain the substances the pathogens require for their growth and reproduction. Instead, the latter need to kill the tissues to release the nutrients that their metabolism demands. Consequently, the defense strategy of the plants is different in each case and completely opposite to that of the pathogens: biotrophic pathogens induce the death of infected cells and confines the infection to a restricted area to maintain cellular life and counteract the attack of necrotrophic organisms (Glazebrook 2005).

Phytohormones participate in the defense against both types of pathogenic microorganisms, and everything indicates that salicylic acid (SA) is the main regulator of the response against biotrophic organisms, while jasmonic acid (JA) and ethylene play a greater role against necrotrophic organisms (Farmer et al. 2003; Vlot et al. 2009).

In response to these functions of phytohormones, pathogens have developed mechanisms to subvert their normal functioning, taking advantage of the existing antagonism between them, such as that between SA and JA. As SA contributes to resistance to biotrophic pathogens, necrotrophic pathogens can activate this path, attenuating that of JA, which gives them advantages of attack. Conversely, biotrophic pathogens trigger the activation of the JA pathway, inhibiting that of SA (Kazan and Lyons 2014).

On the other hand, abscisic acid (ABA), which is known to play an important role in tolerance to abiotic stress, assumes an ambivalent role, interfering at different levels—positively and negatively—with pathogenic signals (Fig. 16.2).

It is believed that this interference in both directions is linked to events as different as the suppression of the resistance conferred by salicylic acid (Mohr and Cahill 2007), the ethylene/JA balance (Anderson et al. 2004), the suppression of Reactive Oxygen Species (ROS), stomatal closure, and the accumulation of callose (Asselbergh et al. 2008). Ton et al. (2009) proposed a model according to which ABA stimulates the defense of the plants in the initial stages of the infection and acts as a suppressor in the advanced stages; however, the large number of contradictory reports on the role of this plant hormone does not yet provide solid explanations about its mode of action.

Consequently, the recognition and response to necrotrophic pathogens are still not sufficiently known, although all these evidences suggest that it is complex in nature and multiple genes and mechanisms are involved, as occurs in the interaction between *Arabidopsis thaliana* x *B. cinerea* (Rowe and Kliebenstein 2008).

The detection of the pathogen's DNA in the host or its products has been useful to diagnose the infection and monitor its progress. Real time-PCR (RT-PCR) (Lievens et al. 2005a; Pasquali et al. 2006) has been useful as a tool for this purpose. However, the presence of the DNA of a fungus in the host is not always an indicator of the infection. For example, the DNA of three strains of *Fusarium oxysporum* (two of them non-pathogenic for tomato) could be detected in plants of this species, even though the symptoms of the infection only appeared where the pathogenic race was present (Validov et al. 2011). However, the amount of fungal DNA detected was several times higher in plants inoculated with the pathogenic race than in plants treated with the two non-pathogenic races, revealing a quantitative relationship that favors the pathogenic microorganism over non-pathogens.

One of the transcription factors of the WRKY family (WRKY33) is involved in the resistance of *Arabidopsis thaliana* to *Alternaria brassicicola* and *B. cinerea* (Zheng et al. 2006; Birkenbihl et al. 2012). The signaling pathway involved is that of ROS; the WRKY family plays an important role in the resistance to numerous types of stress in plants—including the attack of pathogens—(Bakshi and Oelmüller 2014) but also to other physiological phenomena of abiotic origin such as water stress in *Arabidopsis* (Scarpeci et al. 2013), Chinese cabbage (Tang et al. 2014), and cassava (Wei et al. 2016).

Pathogens penetrate the host through stomata (Grimmer et al. 2012), through wounds or by using specialized mechanisms; the accumulation of molecules such as chitin (fungi), flagellin (bacteria), and others such as peptidoglycans and lipopolysaccharides is associated with pathogen attack and proliferation (Grant et al. 2013).

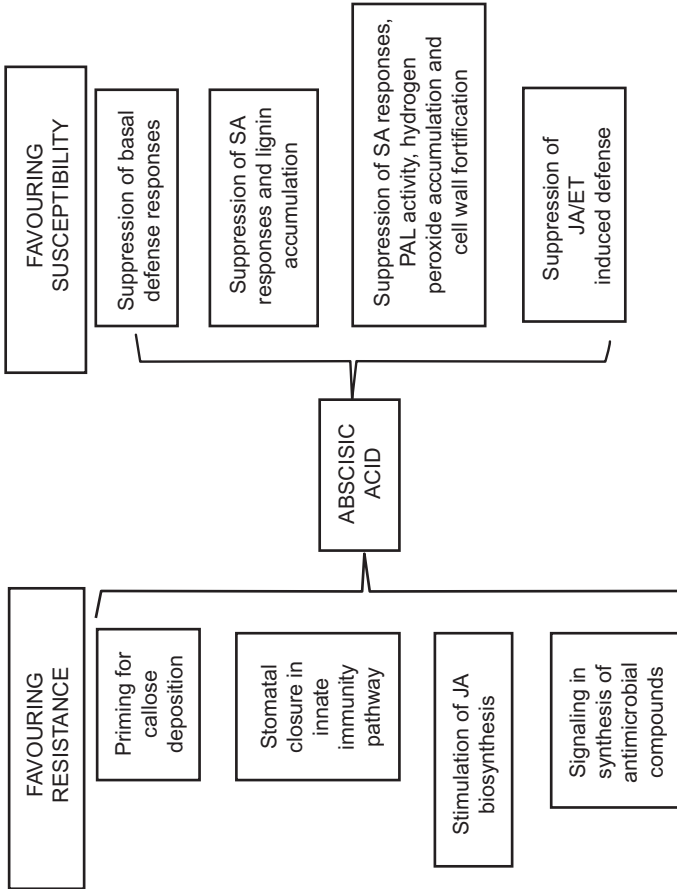


Fig. 16.2 Effects of ABA on plant–pathogen interactions (resumed from results published by Asselbergh et al. 2008)

The penetration of pathogens through stomata is counteracted by the so-called stomatal immunity (Melotto et al. 2006), which is a rapid stomatal closure to restrict the entry of microorganisms. ABA takes part in this closing of the stoma through the control of the hydric balance in the plant (Chater et al. 2014). It has been shown that the mechanism linking ROS and ABA with stomatal closure (Jammes et al. 2009) is related to resistance to *P. syringae* pv tomato DC3000 (Pst) (Jammes et al. 2011). In response to this, some pathogens have mechanisms to overcome the barrier of stomatal immunity. Coronatine, a phytotoxin secreted by some lines of *P. syringae* (Brooks et al. 2004), inhibits stomatal closure (Melotto et al. 2006) promoting the catalysis of SA and preventing its accumulation (Du et al. 2014). Other pathogenic metabolites behave like cytokinins, stimulating the production of ethylene, inhibiting the synthesis of ABA and stomatal closure (Tanaka et al. 2006). Pathogens can also inhibit the ABA-regulated stomatal closure by inducing metabolic processes involving oxalate (Guimaraes and Stotz 2004), triacylglycerol (McLachlan et al. 2016), or starch (Azoulay-Shemer et al. 2016).

As is known, Cl^- , NO_3^- , and malate are the main negative ions balancing K^+ to cause stomatal closure (Kim et al. 2010). In this way, the pathogenic strategy of causing the conversion of malate to oxalate leads to an ionic imbalance favoring potassium and keeping stomata open, facilitating the penetration of the pathogen. On the other hand, a main source of malate is starch, whose accumulation in the cells is related to the stomatal closure. Both events are directly related to each other, and the disturbance of one or the other by the presence of a pathogen could favor the penetration of this through the stoma that would remain open (Azoulay-Shemer et al. 2016).

The studies of McLachlan et al. (2016) in *Arabidopsis* and *Selaginella* (div. *Lycophyta*) showed that for both higher and lower plants, there is a decrease in the content of the lipid droplets present in the guard cells during the stomatal opening. These lipid droplets contain triacylglycerol (TAG), which is presumed to serve as a substrate for obtaining ATP necessary for the process of opening the stomata; in numerous species the presence of TAG in the guard cells has been detected. Lipid compounds play an important role in the defense against the invasive advancement of pathogens from diseased tissues to still healthy tissues (Shimada and Hara-Nishimura 2015). A possible pathway of pathogenic disturbance would be to alter the metabolism of TAG in favor of ATP production, keeping stomata open and favoring penetration.

The losses caused by pathogens are greater, among other factors, because their presence is always detected when the infection is already established in the plantation, through the characteristic symptoms of the disease. If early diagnosis methods could be established, it would be feasible to take much more effective preventive measures. According to Mazarei et al. (2008), and to the response ways that have been discussed above, there are four routes or elements that can be useful in this regard:

- Salicylic acid-induced response.
- Ethylene-induced response.
- Jasmonic acid-induced response.

- The PR1 gene, which in *Arabidopsis* is expressed in the presence of pathogenic infection or the application of substances such as salicylic acid itself (Lebel et al. 1998).

The picture is complex because there are pathogens that do not produce specific toxins, such as necrotrophic fungi and some bacteria. These organisms are characterized by the secretion of a large number of substances that degrade cell walls or counteract the action of host enzymes. Against these actions of the pathogen, effective resistance is low, as well as recognition through the PTI and ETI processes. Some toxins, in addition, can be recognized by the host, but this recognition does not go in the sense of resistance but in that of susceptibility (Friesen et al. 2008).

Finally, attention should be paid to the existence of beneficial microorganisms that act symbiotically with the plant. This phenomenon is particularly interesting because both pathogenic and symbiotic microbes have conserved sites of similar microbial molecular patterns (MAMPs) (Zamioudis and Pieterse 2012). The rhizobacteria have developed mutations of the MAMPs that prevent their recognition by the defensive systems of the plant (Trdá et al. 2014). In any case, the particular characteristics of the interaction between the host and the pathogen, and the nature of the molecular signals that are exchanged for mutual recognition and the establishment of defensive reactions in the host, must be taken into account to establish diagnostic techniques using nanotechnology.

16.2 Nanodiagnosics for Fungal Plant Pathogen

In global agriculture, phytopathogenic fungi are responsible for pre- and post-harvest diseases in several crops and they are responsible for quantitative losses; the damage they cause not only refers to economic losses of production but also to losses in biological production, that means, the alteration produced in the growth and development of the host plants attacked by these microorganisms (Agrios 2005).

Both bacteria and fungi cause high crop losses; however, fungal species are often the cause of pathological deterioration of fruits, leaves, stems, roots, tubers, among others. Some authors estimate that these losses are between 5 and 25% in developed countries and between 20 and 50% in developing countries (FHIA 2007).

The effects of fungi on plants can be local, when they affect a small portion of the tissue, or general if the damage is in the whole plant. The damage caused by the fungi is primarily necrosis (death of the tissue they infect), atrophy of the whole plant or parts, or overgrowth (García 2004).

The protection of economical crops is important to meet the demand of a growing world population for the production of food (Strange and Scott 2005). Plant pathogens (fungi, viruses, bacteria, nematodes) are responsible for direct yield losses ranging between 20 and 40% of global agricultural productivity (Oerke et al. 1994; Oerke 2006); for this reason the early detection of diseases is important to avoid disease spread with minimal loss to crop production (Sankaran et al. 2010; Martinelli et al. 2014).

Traditionally, the methods for the identification of plant pathogens are based on visual symptoms in the field and *in vitro* culture of the pathogen for morphological identification, these lead to mistake because they are not sensitive and they consume a lot of time and money. These methods depend on the experience of the person that makes the diagnosis (Fig. 16.3) (Sankaran et al. 2010; Kashyap et al. 2011). Some other identification methods more sensitive and useful for diagnosis include:

16.2.1 Polymerase Chain Reaction (PCR)

In 1983, Kary Mullis, PhD, a scientist at the Cetus Corporation, conceived of PCR as a method to copy DNA and synthesize large amounts of a specific target DNA. This technology allows the amplification of an original DNA strand and as a result, many copies are obtained. By the use of specific primers, pathogens can be identified quickly and precisely. In addition, a reverse transcription PCR has been used for pathogen detection in a very sensitive way (López et al. 2003). PCR can be affected by the quality of the DNA extracted, primers design that must be specific for the diseases or pathogen and necessary to initiate the reaction, enzyme activity (polymerase), buffer and concentration of deoxynucleoside triphosphate (dNTPs) (Schaad and Frederick 2002; Van der Wolf et al. 2001).

- Usually for primer design conserved genes are selected to amplify conserved regions, for fungi analysis the ITS (internal transcribed spacer) region of the rDNA is widely used. This region has conserved areas suitable for primer designing, also it has variable areas that allow discrimination over a wide range of taxonomic levels (ITS region) (White et al. 1990). The ITS is an ubiquitous region and it is present in all eukaryotic organisms. In some studies about fungal taxonomy, this ITS region has been used showing difference between species such as *Pythium ultimum* and *P. helveticum* (Kageyama et al. 2007); *Peronospora arborens* and *P. cristata* (Landa et al. 2007); *Colletotrichum gloeosporioides* and *C. acutatum* (Kim et al. 2008), and within species e.g., allowing differentiation of

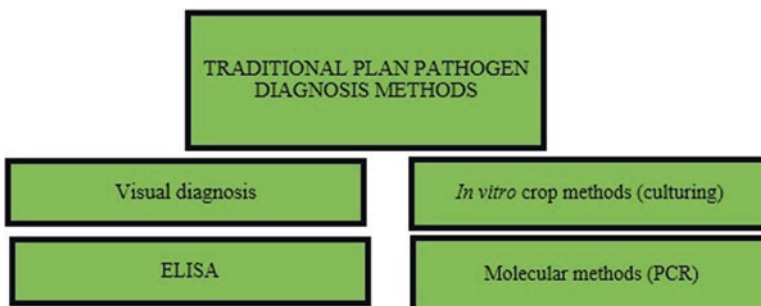


Fig. 16.3 Some traditional methods used for plant pathogen diagnosis

Puccinia striiformis f. sp. tritici (Zhao et al. 2007). Some other examples where the ITS region was used to design primers for fungi identification are *Sclerotium rolfsii* (Jeeva et al. 2010) and *Colletotrichum capsici* (Torres-Calzada et al. 2011).

- Some mitochondrial genes such as cytochrome oxidase genes (*cox*) can be used for fungal identification (Martin and Tooley 2003; Powers 2006) because similar to ribosomal genes they are present in high copy number and present in both rapidly evolving and conserved regions. Some pathogen species cannot be identified with certain primers. For example, certain *Phytophthora* species are impossible to identify using ITS sequences and others are not distinguished using mitochondrial *cox II* genes (Cooke et al. 2000; Martin and Tooley 2003).

16.2.2 Enzyme-Linked Immunosorbent Assay (ELISA)

The ELISA is an immunological test used to measure antibodies, antigens, proteins, and glycoproteins in biological samples (Clark and Adams 1977) with target antigens from the viruses, bacteria, and fungi that will bind specifically with antibodies conjugated to an enzyme. The detection is based on changes of color due to the interaction between the substrate and the immobilized enzyme (Gorris et al. 1994; López et al. 2001).

- The identification of *Cladosporium fulvum*, a potentially serious fungal pathogen of tomato, can be made based in the expression of β -glucuronidase gene (GUS) that can be measured for detection and quantification of biomass in tomato leaves. This method was compared with plate-trapped antigen (PTA)-ELISA showing that both methods could detect the pathogen in a low level ($<1 \text{ mg g}^{-1}$) (Karpovich-Tate et al. 1998).
- The fungal pathogen *P. ultimum* causes the damping-off and root rot diseases of hundreds of diverse plant hosts including corn, soybean, potato, wheat, fir, and many ornamental species (Farr and Rossman 2014), and 188 isolates were identified as *P. ultimum* at the asexual stage based on morphological characteristics and their positive reaction with E5 antibody in ELISA (Yuen et al. 1993).

16.2.3 Immunofluorescence

It is a technique used for light microscopy with a fluorescence microscope and is used primarily on microbiological samples. This technique uses the specificity of antibodies to their antigen to target fluorescent dyes to specific biomolecule targets within a cell, and therefore allows visualization of the distribution of the target molecule through the sample. This technique is used to analyze microbiological samples, also to identify or detect pathogen infections in plant tissues (Ward et al. 2004). One example is the detection of *B. cinerea* that induce infection in onion seed heads and cause brown stain (Dewey and Marshall 1996).

16.2.4 Flow Cytometry (FCM)

It is an optical technique laser-based with several applications including the counting of cell and sorting, the detection of some biomarkers, and protein engineering. This technique is interesting because several parameters can be detected simultaneously. FCM was first used in bacteria to study the kinetics cycle of several cells, antibiotic susceptibility, for counting, for DNA characterization, also to characterize fungal spores, but still is a new methodology for plant pathogen identification (Chitarra and van den Bulk 2003).

For plant fungal diseases, FCM is used to characterize genome sizes of fungal and oomycete populations, several pathogen detection, and the monitoring of the viability, cultivability, and gene expression (D'Hondt et al. 2011).

16.2.5 Fluorescence Imaging

It is based in the fluorescence of chlorophyll on leaves and when fluorescence parameters change the pathogen infection can be analyzed based in the photosynthetic apparatus and photosynthetic electron transport reactions (Kuckenberg et al. 2009; Bürling et al. 2011). In plant fungal pathogen leaf rust and powdery mildew infections in wheat leaves at 470 nm were precisely detected with the analysis of temporal and spatial variations of chlorophyll fluorescence (Kuckenberg et al. 2009). At present the practical application of this technique directly in the field is limited (Chaerle et al. 2009; Cséfalvay et al. 2009).

16.2.6 Hyperspectral Techniques

These techniques are highly robust and use spectrum in a range of 350 to 2500 nm to obtain important information about plant condition. In addition, with these techniques the study of plant phenotype and the identification of crop diseases can be made (Mahlein et al. 2012). In the case of plant disease detection, measuring the changes in reflectance resulting from the biophysical and biochemical characteristic changes upon infection has been applied to identified *Magnaporthe grisea* infection of rice, *Phytophthora infestans* infection of tomato, and *Venturia inaequalis* infection of apple trees (Zhang et al. 2003; Delalieux et al. 2007).

The combination of molecular diagnosis and nanotechnology is a great technology for the rapid and precise identification of different plant pathogens. At present for diagnosis, several nanodevices and nanosystems have been used, as well as sequencing of DNA individual molecules. The recently developed nanomaterials with special nanoscale characteristics represent a tremendous advance in the technology of detection and diagnosis of plant pathogens (Khiyami et al. 2014).

The combination of biology and nanotechnology is called nanobiosensors (Yang et al. 2008), and they can increase greatly sensitivity and consequently when a disease problem is present in a crop they can diminish response time (Small et al. 2001). For these reasons, nanosensors can improve production and food safety in agriculture. In this context, Dubas and Pimpan (2008) investigated the particular optical properties of silver nanoparticles, the interaction between silver nanoparticles and sulphurazon-ethyl herbicide. The authors found that these nanoparticles increased concentrations of herbicide in a solution and induced a variation in color of the nanoparticles from yellow to orange red and finally to purple; this variation is useful for the detection of several contaminants such as organic pollutants and microbial pathogens in water bodies and in the environment (Pal et al. 2008).

16.2.7 Nucleic Acid Based Affinity

Biosensor is a new method for pathogen detection that allows the detection at molecular level of the diseases before any symptoms appear and this has been widely used for detection of bacteria, fungi, and genetically modified organisms. A single-stranded DNA (ssDNA) is the most used DNA probe on electrodes to measure hybridization between probe DNA and the complementary DNA analyses (Eun and Wong 2000). There are four major types of DNA-based biosensors depending on their mode of transduction: optical, piezoelectric, strip type, and electrochemical DNA biosensors. The optical DNA-based biosensors can be further classified to three subtypes—molecular beacons (MB), surface plasmon resonance (SPR), and quantum dots (Eun and Wong 2000).

- (a) The molecular beacons (MB) is a new fluorescence probe based on DNA.
- (b) The surface plasmon resonance (SPR).
- (c) Quantum dots (QD) are semiconductors that use nanocrystals and light of specific wavelengths based in a luminescent property of the infrared light emitted (Fig. 16.4) (Edmundson et al. 2014). This technology is better than other fluorescent dyes because luminescence is more efficient, the spectra emission is small, and great photostability QD can be excited to all colors with only one light source (Warad et al. 2004). QD have been used for diagnosis of plant pathogens such as fungi. In yeast was first reported the mycosynthesis of semiconductor nanomaterials because yeast can produce cadmium sulfide (CdS) crystallites in response to cadmium salt stress (Dameron et al. 1989), but yeast is not the only microorganism that can produce CdS; nevertheless, the studies on their fluorescent properties are not enough (Yadav et al. 2015). *Fusarium oxysporum* Schltdl. can produce a myco-mediated synthesis of highly fluorescent CdTe quantum dots when reacted with a mixture of CdCl₂ and TeCl₂ (Jain 2003; Kashyap et al. 2013; Alghuthaymi et al. 2015). Another example is the use of QD-FRET (Fluorescence resonance energy transfer) mechanism (Grahl and Märkl 1996) for detection and identification of *Aspergillus amstelodami* in concentrations as low as 10³ spores/mL in 5 min or less (Kattke et al. 2011).

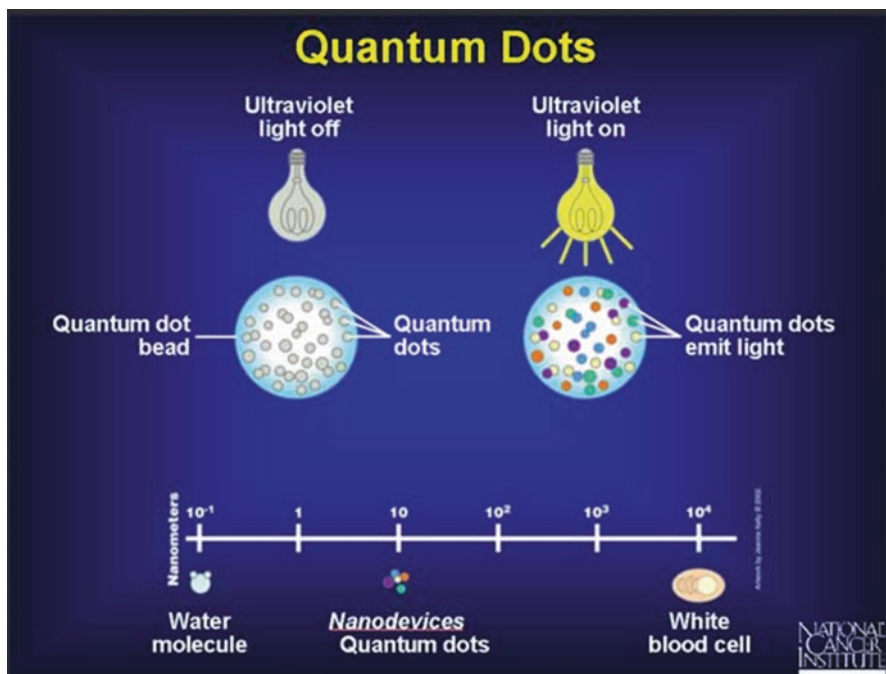
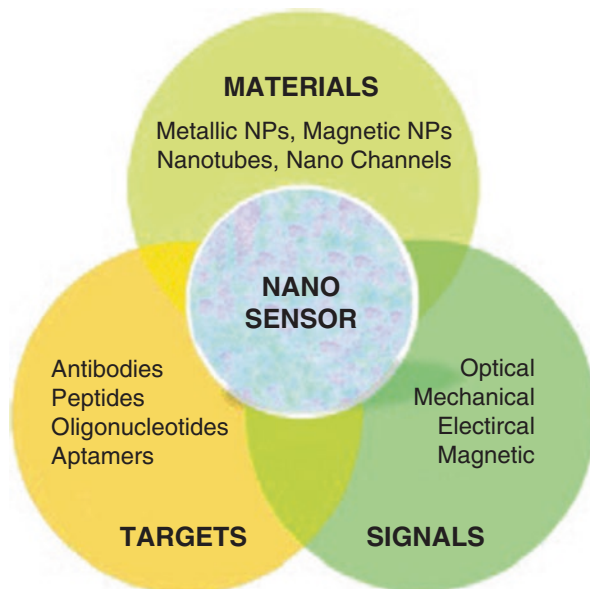


Fig. 16.4 Quantum dot schematization. (www.ubooks.pub/BOOKS/BO/E20R2020/MAIN/images/image014jpg)

Nanomaterials have been used for sensor development because they offer a friendly platform that can be utilized for the assembly of bio-recognition elements, the high surface area, high electronic conductivity and plasmonic properties of nanomaterials that enhance the limit of detection. Several metal and metal oxide nanoparticles, quantum dots, carbon nanomaterials such as carbon nanotubes and graphene as well as polymeric nanomaterials are used for biosensor construction (Singh et al. 2010).

Nanosensor is another technique used for the detection of plant pathogens in a very precise way (Fig. 16.5) (Esker et al. 2008; Rai and Ingle 2012). Several polymers such as polyaniline, polythiophene, and polypyrrole are used for sensors fabrication for the detection of molecular signal (Sekhon 2010), so these bio-nanosensors can improve sensitivity and reduce significantly the response time to discover potential disease problems and they were used in agriculture and food system to detect and quantify small amounts of pathogens like viruses, bacteria, and fungi (Rai and Ingle 2012). These nanosensors can be used in real time by the connection to a GPS, monitoring not only diseases but also soil conditions and crop health (Clarke et al. 2009; Rai and Ingle 2012). Nanosensors can allow scientists and farmers to identify plant diseases before visible symptoms appear and this will facilitate their control with enough time to avoid economic losses (Rai and Ingle 2012).

Fig. 16.5 Nanosensors.
Swierczewska et al.,
(2012)



Nanosensors also can be used to detect some chemicals released during food spoilage and some of them are based on microfluidic devices (Baeummer 2004), so they can be used to identify pathogens proficiently in short time with high sensitivity.

A sensor with gold electrode and copper nanoparticles has been used to monitor the levels of salicylic acid in oil seeds to detect *Sclerotinia sclerotiorum* (Wang and Li 2010).

Biosensors combined with copper oxide (CuO) nanoparticles were used for detecting *Aspergillus niger* (Etefagh et al. 2013). *A. niger* causes black mold of onions and ornamental plants. Infection of onion seedlings can become systemic, manifesting only when conditions are conducive. *A. niger* causes a common post-harvest disease of onions, in which the black conidia can be observed between the scales of the bulb. The fungus also causes disease in peanuts and grapes (Schuster et al. 2002).

Several biosensors have been developed and described for mycotoxin analysis, some of them have the potential of multi-array mycotoxins identification with the principal role of decreasing the time for fungal pathogen detection (Baeummer 2004).

Nanoparticles have been used for the detection/diagnosis of fungal plant pathogens by several authors (Boonham et al. 2008; Yao et al. 2009). Some examples are gold nanoparticles, copper oxide, titanium dioxide, tin dioxide, and some others.

Partial charcoal is the wheat and triticale disease caused by the fungus *Tilletia indica* Mitra, also known as *Neovossia indica* (Mitra) Mundkur. Typically, the fungus infects only a few grains per spike and the disease only develops in a part of the infected grains. The disease is also known as Carnal Charcoal, and it was discovered in 1931 in India. Subsequently, it has been found in large areas of northern India, Pakistan, Nepal, Iran, and in some parts of Mexico and South of the United States (Vernon and Vizcarra-Mendoza 2000). Gold nanoparticles have been devel-

oped for detecting *T. indica* using surface plasmon resonance (Singh et al. 2010). These nanoparticles have a high electroactivity and electronic conductivity (Cao et al. 2011).

In plants infected with pathogenic fungus *Phytophthora cactorum*, nanoparticles of TiO₂ or SnO₂ on screen-printed carbon electrodes have been used for the identification of p-ethylguaiaicol, a volatile compound present in this plants (Fang et al. 2014). *P. cactorum* was first identified on cacti in 1870 by Lebert and Cohn (Erwin and Ribeiro 1996). This oomycete is capable of infecting an extremely large number of hosts (Erwin and Ribeiro 1996; Benson and Jones 2001) and is problematic in low-lying or wet field conditions. It can limit production for many economically important crops such as apple, pear, rhododendron, azalea, and strawberry (Fujita 1990; Erwin and Ribeiro 1996). *P. cactorum* can cause root, collar, and crown rots, as well as foliar and fruit infections.

A briefcase-sized kit is used as another method of nanodiagnosis directly in the field and it contains some measuring devices, reagents, power supply, and other products (Goluch et al. 2006). By using nanodiagnostic kit equipment potential plant pathogens could be detected easily and quickly and this will allow to prevent farmers from potential diseases (Pimentel 2009). For example, 4mycosensor is an antibody-based assay for the real-time detection of ZEA, T-2/HT-2, DON, and FB1/FB2 mycotoxins on the same single strip in corn, wheat, oat, and barley samples at or below their respective European maximum residue limits (MRLs) (Lattanzio et al. 2012), so this immunoassay is fast, cheap, easy-to-use, and suitable for the purpose of quick screening of mycotoxins in cereals.

Another tools used for nanodiagnostic in plant pathology are magnetic nanoparticles (MNPs) consisting of magnetite (Fe₃O₄) and they were produced with hydrothermal protocols. The size and distribution of these particles were characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS), which revealed that the synthesized MNPs were highly monodispersed. The MNPs were used by Alghuthaymi (2017) for the molecular identification of two novels *Cladosporium cladosporioides* from tomato phylloplane; for this reason fungal DNA was extracted using MNPs in comparison with the conventional sodium dodecyl sulfate (SDS) method in the context of quality, quantity, and timing process. For PCR the universal primers ITS for fungi were used together with actin genes as housekeeping ones and the amplification result was 100% demonstrating the high quality of the isolated DNA. In this study, 47 isolates of *C. cladosporioides* complex were phylogenetically evaluated based on DNA sequences of the internal transcribed spacer regions ITS1 and ITS2 together with partial actin and translation elongation factor 1- α gene sequences. The *Cladosporium* strains were isolated in Saudi Arabia and Egypt from tomato crop and were identified as *C. asperulatum* and *C. myrtacearum* based on their molecular phylogenetic characteristics. The combination of magnetic nanoparticles and DNA isolation could be used commonly both in plant pathology laboratories and in the nanobiotechnology industry (Alghuthaymi 2017). Methods relating with magnetic separation have been extensively studied, but still there is a need for an efficient technique to isolate DNA for

diagnostic applications with high sensitivity and MNP techniques use less steps, microcentrifuge tubes and time; for all these reasons, it is more cost-effective when compared with traditional techniques (Maeda et al. 2016).

16.3 Plant Viruses: Nanodiagnostic

16.3.1 Viruses

Viruses are pathogens that have one or two molecules of nucleic acids, surrounded by a protective layer, consisting of proteins. Ninety percent of the viruses have an RNA genome and the remaining 10% have a DNA genome, single-stranded or double-stranded. These biological entities are considered obligate parasites and they have the capacity to cause diseases in all living organisms, including man. Plant viruses cause the damage inside plant cells by intervening the allocation of resources that the plant has produced through photosynthesis, causing a delay in growth, and shortening the life of the host; however, other observed symptoms include chlorosis, yellowing, crinkling, mosaics, mottled, necrosis, deformation of leaves and fruits, and flower abortion, resulting in a severe impact on production. However, some viruses, under appropriate conditions, can infect a plant without producing symptoms of disease (Bové et al. 1988; Hull 2002; Agrios 2005; van der Want and Dijkstra 2006; Schuman and D'Arcy 2010).

Viruses are ranked as the second most important plant pathogens following fungi. Economic loss has been estimated more than several billion dollars per year worldwide in many crops such as barley, corn, potato, rice, and wheat. The crop damages owing to viral diseases are difficult to predict, because they depend on virus strain, host plant cultivar/variety, region, and time of infection (Hull 2002; Agrios 2005; Strange and Scott 2005; Ellis et al. 2008).

In addition, plants can develop symptoms similar to those produced by this group of phytopathogens when they are affected by biotic or abiotic factors such as nutritional imbalances, unfavorable weather, and pathogens caused by pests and other agents. Therefore, the diagnosis of viral diseases based on the observed symptoms is more difficult than those caused by other pathogens (Lievens et al. 2005b; van der Want and Dijkstra 2006).

16.3.2 Nanodiagnosis Applied to Virology

The diagnosis is the basis to manage plant diseases and to predict the crop loss by infection of plant pathogens. The main problem in the productivity of a crop lies mainly in the early detection of the disease or infectious agent. Most of the time,

pesticides are applied preventively, causing residual toxicity in the crop in addition to environmental risks. On the other hand, the application of pesticides once the disease is presented cause an extra economic investment in crop management. Within the diseases, the viral ones are the most complicated to control due to the emphasis in the control of their vectors and consequently their propagation. Therefore, the key to success in the control of diseases based on a crop management system, particularly of viral origin, is to figure out the causes by the detection in early stages such as the replication of viral DNA or the initial production of its viral protein (Pearson et al. 2006; van der Want and Dijkstra 2006; Aboul-Ata et al. 2011).

The viral diagnosis based on nanomaterials and utilization of biomarkers including the development of multiple diagnostic kits has been of great importance to detect the variants and identify differential proteins production in healthy and sick states during the infectious cycle to stop the disease. These nano-based diagnostics not only increase the speed of detection but also increase the power of the detection (Prasanna 2007; Mousavi and Rezaei 2011; Rai and Ingle 2012).

Methods for detection and identification of viruses are critical in the management of these phytopathogens (Aboul-Ata et al. 2011). Therefore, detection methods should be more convenient, effective, specific and permit the use for detecting plant pathogens (McCartney et al. 2003). Nanotechnology is the creation and utilization of materials, devices, and systems through the control of matter on the nanometer-length scale, at the level of atoms, molecules, and supramolecular structures. It is the popular term for the construction and utilization of functional structures with at least one characteristic dimension measured in nanometers (Jain 2003; Tan et al. 2004). A rapid diagnosis of the disease often depends on the sensitivity of the genes used for the detection, identification, and control of smaller and less abundant targets (mRNA, DNA, proteins, and peptides) (Wang et al. 2006).

16.3.2.1 Field Sensing Systems Based in Nanosensors

This system of precision agriculture is used to monitor the appropriate time of planting and harvesting in the field, climatic conditions, efficient use of water and soil nutrition, as well as the detection of pests, including viruses. Field system makes use of nanomaterials such as polyaniline, polythiophene, and polypyrrole that function as a network of wireless sensors with global positioning system for real-time monitoring and satellite imagery in the field (Joseph and Morrison 2006; Derosa et al. 2010; Chen and Yada 2011; Ingale and Chaudhari 2013; Prasad et al. 2014, 2017).

Nanosensors identify plant diseases before visible symptoms appear and thus facilitate their control. Precision farming will allow improved agriculture production by providing precise data, helping growers to make better decisions (Rai and Ingle 2012).

16.3.2.2 Nanobiosensors as a Diagnostic System

Nanobiosensors are nanosensors with immobilized bioreceptor probes that are selective for target molecules which offer the advantage of being portable, small, quantitative, and reliable in the identification of potential disease problems. These systems are used in agriculture for the detection and quantification in minutes of pathogens such as viruses (Rai and Ingle 2012; Khiyami et al. 2014; Srinivasan and Tung 2015). These sensors can be linked to a GPS and distributed throughout the field for real-time monitoring of disease, soil conditions, and crop health (Nezhad 2014; Prasad et al. 2014, 2017).

Nanowire biosensors are a class of nanobiosensors, of which the major sensing components are made of nanowires coated by biological molecules such as DNA molecules, polypeptides, fibrin proteins, and filamentous bacteriophages. Since their surface properties are easily modified, nanowires can be decorated with virtually any potential chemical or biological molecular recognition unit, making the wires themselves analyte independent. Nanomaterials, due to their unique characteristics, including stable emissions and size-dependent properties, have attracted great attention as they transduce the chemical bonding event on their surface to a change in the conductance of the nanowire in an extremely sensitive, real-time and quantitative manner (Rai and Ingle 2012; Kashyap et al. 2017).

Nanowires were used as a transducer biosensor to detect cucumber mosaic virus (CMV) and papaya ring spot virus (PRSV), indicating that nanowires are good candidate materials for the manufacture of nanoscale biosensors for the diagnosis of viral diseases (Ariffin et al. 2014). Also, 11-mercaptopundecanoic acid was self-assembled on gold surface and then crosslinked with anti-maize chlorotic mottle virus (anti-MCMV) for MCMV disease detection. SPR response to MCMV solutions was evaluated over time with different concentrations from 1 to 1000 ppb. The limit of detection was evaluated to be approximately 1 ppb (Zeng et al. 2013).

Biosensors based on living cells are characterized by low limit of detection, high specificity, and rapid response time. A novel portable cell biosensor system for detection of potato virus Y (PVY), CMV, and tobacco rattle virus (TRV) was fabricated by immobilizing the vero cells carrying virus specific antibodies on their membranes. This study demonstrated an important step towards the development of a portable plant virus detection system suitable for on-field application (Perdikaris et al. 2011).

16.3.2.3 Nanodiagnosis Using Quantum Dots (QDs)

QDs, as described above in detail, are semiconductors made out of the elements from groups II and VI or groups III and V in periodic table that fluoresce when stimulated by an excitation light source. Furthermore, QDs are inorganic fluorophores presenting major advantages over traditional organic fluorophores used as markers on nucleic acids or proteins for visual detection and these nanomaterials have been most widely used for disease diagnosis (Wang et al. 2006; Adams and Barbante 2013; Holzinger et al. 2014). In the most of the cases, viral nucleic acids have been used for

hybridization assays as well as antigen-antibody affinity for building immunoassays as mechanism, which will enable FRET follow their detection. FRET is an acronym for Förster resonance energy transfer and involves non-radiative transfer of energy between donor and acceptor fluorophores (Uhl et al. 2011).

Quantum Dots FRET-based biosensors are applied in the detection of viruses like necrotic yellow vein virus (BNYVV), a plant virus responsible for rhizomania disease in sugar beet and transmitted by *Polymyxa beta* (Keskin). BNYVV sensor FRET occurred between thioglycolic acid-modified cadmium telluride QD conjugated with anti-glutathione-S-transferase antibody (anti-GST) via electrostatic interaction as energy donor and fluorescent dye rhodamine attached to GST as energy acceptor (Safarpour et al. 2012).

Likewise, the nanodiagnostic of *citrus tristeza virus* (CTV) was reported where the cadmium telluride-quantum dots (CdTe-QDs) were conjugated with a specific antibody against coat protein (CP) of CTV, and the CP was immobilized on the surface of gold nanoparticles (AuNPs) to develop a specific and sensitive fluorescence resonance energy transfer (FRET) based nanobiosensor (Shojaei et al. 2016a). This was also done in another study; however, the conjugated was immobilized on the surface of carbon nanoparticles (CNPs). The limit of detection was measured at about 220 ng mL⁻¹ of CTV (Shojaei et al. 2016b).

In the same way, the conjugated CdTe-QDs-CP of CTV was achieved in a parallel reaction, rhodamine dye molecules were attached to the purified recombinant CTV-CP. Two independent approaches were explored for detection of the infected plants. First, in fluorescence resonance energy transfer (FRET) based assay, the quenching ability of rhodamine molecules was applied for altering the QDs light emission. More specifically, donor-acceptor complexes (Ab-QD + CP-Rd) were created based on the affinity of antibody-antigen molecules. The resulting assembly brought Ab-QD (the donor) and the Rd-CP (the acceptor) into a close proximity and resulted in a substantial decrease in the intensity of QD light emission. Addition of free antigen into the solution resulted in the replacement of CP-Rd with free CP and a subsequent increase in the emission of QDs. In the second approach, a non-FRET based assay was performed through the addition of free antigen to the Ab-QD solution, which led to the aggregation of the Ab-QD conjugates and consequently to a significant increase in the light intensity emission of the QD (Safarnejad et al. 2017).

16.3.2.4 Gold Nanoparticles

Gold nanoparticles (GNP) are used in biosensors due to their optical, electronic, compatibility and simple modification properties. These nanomolecules have been in active use in the identification of chemical and biological agents (Li et al. 2010; Biju 2014). Predominantly, transmission electron microscopy has historically remained the predominant means to detect biospecific interactions using colloidal gold particles (Hayat 1989). In addition to the conventional colloidal gold with quasi-spherical particles (nanospheres), also nonspherical particles, such as nanorods, nanoshells, nanocages, nanostars, among other particles can be used (Khlebtsov and Dykman 2010).

In this regard, it was reported the use of DNA molded to self-assembly of gold nanoparticles grouped in different configurations for the colorimetric detection of the DNA of the Tomato leaf curl New Delhi virus (ToLCNDV), using a bifunctional oligonucleotide probe conjugated with gold nanoparticles. This study provided new insight into the preparation of gold nanoparticle clusters in defined shapes and sizes using a single type of GNP (Dharanivasan et al. 2016). Likewise, another report indicated the detection of tobacco mosaic virus (TMV) through immunochromatography technique for express diagnosis of plant viral infections on polycomposite test strips using colloidal gold nanoparticles as a visual label. In this work, polyclonal antibodies were used whose molecules can differ significantly in chemical composition and immunochemical and physicochemical properties (Drygin et al. 2009).

In other work, a highly practical and rapid lateral-flow assay (LFA) was developed for the detection of soybean mosaic virus (SMV). The LFA is an immunoassay method based on immuno-chromatography. In this research, they used gold nanoparticles for colloidal solution. The assay can be used to detect SMV in infected leaf samples and soybean seeds (Zhu et al. 2016).

16.3.2.5 Nanorod Technology

Gold nanorods (AuNRs) have larger absorption and scattering cross sections in the l-mode PPR wavelength region than AuNSs in their PPR wavelength region (Parab et al. 2010; Lin et al. 2012). The l-mode PPR wavelength is tunable from the visible to near-infrared regions (650–900 nm) by tailoring the aspect ratio of AuNRs. The spectral region is particularly useful for biosensing because within the range the background absorption and scattering of endogenous chromophores from biological mixtures (e.g., hemoglobins in blood) are minimal (Nusz et al. 2008). In particular, AuNRs have inherently higher sensitivity to the local dielectric environment than similar sized nanospheres (McFarland and Van Duyne 2003). Moreover, the l-mode PPR of AuNRs has higher bulk refractive index (RI) sensitivity and also narrower line width than the t-mode one (Ni et al. 2008).

Due to the unique optical properties of AuNRs, they have been recently developed to be highly sensitive optical transducers for nanodiagnosis, such as being probes for detecting target DNA of pathogenic bacteria (Parab et al. 2010; Wang et al. 2012) and Raman labels in sandwich immunoassay for detection of virus (Baniukevic et al. 2013). Based in the AuNR functionalized by antibodies, the detection of *cymbidium mosaic virus* (CymMV) or *odontoglossum ringspot virus* (ORSV) using fiber optic particle plasmon resonance immunosensor was recorded (Lin et al. 2014). These viruses were also detected in crude saps using the quartz crystal microbalance (QCM) technique with gold electrodes on either side immunosensor which measures the change in frequency of a quartz crystal resonator (Eun et al. 2002).

16.3.2.6 Nanoribbon Technology

The chemiresistive immunosensor based on antibody-functionalized polypyrrole (PPy) nanoribbons was used to detect viral plant pathogen (James 2013). In the study, CMV detection was reported, where lithographically patterned nanowire electrodeposition (LPNE) technique was employed to batchfabricate the PPy sensor by integrating patterned microelectrodes. For it, *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide (EDC)/*N*-hydroxysuccinimide (NHS) was used to surface functionalize antibodies for CMV onto the nanostructured PPy. It is important to mention that in this study the detection was optimized by adjusting the electrical conductivity of PPy nanoribbons, the dimensions of the nanostructure, and the ionic strength of the pH buffer (Chartuprayoon et al. 2013).

16.3.2.7 Immunosensors

This technique consists of antibodies (Ab) or antigens (Ag) coupled to a transducer that generate an analytical response, and it can provide an alternative to used detection system. Depending on the method of signal transduction, immunosensors may be divided into four basic groups: electrochemical, optical, piezoelectric, and thermometric. Among these different types of immunosensors, the electrochemical ones show more potential thanks to their higher sensitivity, higher speed, and permanent control (Ricci et al. 2007; Hassen et al. 2011; Sun et al. 2011).

In relation to it, a portable electromechanical immunosensor system was performed for the detection of CMV, based on immobilized CMV specific antibodies conjugated with gold nanoparticles. This immunosensor provides a promising successful tool for real-time and sensitive CMV detection in the nanophytopathology (Rafidah et al. 2016). Also, recently a label-free and sensitive electrochemical immunosensor for efficient and rapid detection of CTV was performed. The specific antibody against coat protein (CP) of CTV was successfully immobilized on 11-mercaptopundecanoic acid (MUA) and 3-mercapto propionic acid (MPA) modified gold electrode via carbodiimide coupling reaction using *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC) and *N*-HydroxySuccinimide (NHS) (Haji-Hashemi et al. 2017).

Capsicum chlorosis virus (CaCV) was detected efficiently in bell pepper by sensitive label-free amperometric-based biosensor. Antigen was immobilized over the surface of gold nanoparticle/multi-walled carbon nanotube (Nano-Au/CMWCNT) screen-printed electrodes using 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC)/*N*-hydroxysuccinimide (NHS) crosslinking chemistry followed by interaction with groundnut bud necrosis virus (GBNV)/CaCV specific polyclonal antibody (Sharma et al. 2017).

16.3.2.8 Nanochips

Based on an electronically addressable electrode, the nanochips are kinds of micro-arrays, which consist of fluorescent oligo capture probes that are used to identify hybridization. This nanotechnology is highly specific and sensitive to detect the single nucleotide changes occurring in bacteria and viruses. A particular feature of this system is that biotinylated immobilized molecules can be either oligo capture probes or amplified PCR samples (Sosnowski et al. 1997; López et al. 2009). Due to their ability to discriminate single nucleotide changes, nanochips have shown high specificity and accuracy to diagnose PVY, potato virus X (PVX), and potato leafroll virus (PLRV) in potato. In addition, the Nanogen system allows differentiating between the PVY, PVY⁰, and PVY^{N/NTN} races (Ruiz-García et al. 2004).

In the management of viral diseases, preventive control is efficient when the crop is free of viruses; therefore, a quick, accurate and effective diagnosis is of vital importance. In this sense, the diagnosis based on symptoms is not entirely effective, since these can be associated with nutritional deficiencies and interactions between hosts and viral co-infections. For this reason, the different nanodiagnostic technologies can be applied depending on the purpose of the investigation. Under this premise, it is necessary to continue conducting research to optimize these tests in order to obtain reliable results when the pathogen is in low titers in its host.

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Chapter 17

Nanocrystalline Cellulose: Production and Applications



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17.1 Introduction

Cellulose is an abundant renewable resource which can be used for a number of applications. It is mainly found in plant cell wall and plays a vital role in maintaining its structure. Besides plants, cellulose is also found in fungi, bacteria, and some tunicates (George and Sabapathi 2015). Cellulose is a fibrous and linear natural polymer consisting of glucose units bound by β -1,4-linkages with a degree of polymerization ranging from 10,000 to 15,000 units depending on the type of biomass (Sjostrom 1993). For more than a century, several applications of cellulose in food, pharmaceuticals, polymer, pulp, and composite industries have been studied (Coffey et al. 1995; de Souza Lima et al. 2003). Agricultural waste such as rice straw, sugarcane bagasse, sawdust, cotton stables, and woody forest residues are the main source of cellulose for various applications in industries. Production of Nano-Crystalline Cellulose (NCC) is one of the products being evaluated for a number of applications in recent years. NCC produced from

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cellulose fibers are regarded as nanobiomaterial with variety of applications in chemicals, food, pharmaceuticals, etc. (Habibi et al. 2010).

NCC is produced by breaking the natural polymer of cellulose and separating the crystalline section. The general steps involved in the production of NCC from various sources of biomass were illustrated in Fig. 17.1. Nanocrystalline celluloses are typically 5–70 nm in width and 100 nm to several micrometers in length. NCCs (referred to as whiskers) can be classified based on their dimensions, functions, and preparation methods. NCC has many useful characteristics compared to cellulose such as its physicochemical properties including high surface area, specific strength, and optical properties (Peng et al. 2011). Various studies in literature have reported the chemical structure, physical and mechanical properties of NCC (de Souza Lima and Borsali 2004; Peng et al. 2011; Huq et al. 2012). The biocompatible and biodegradable nature of NCC makes it ideal for several applications and is thus the focus of considerable research. Developing commercial scale methods to produce nanocrystalline cellulose from the forest-based biomass can certainly contribute to the advancement of biobased industries around the world. In this chapter, we have highlighted the important production methods, modification, applications of NCCs, and the economics of its production.

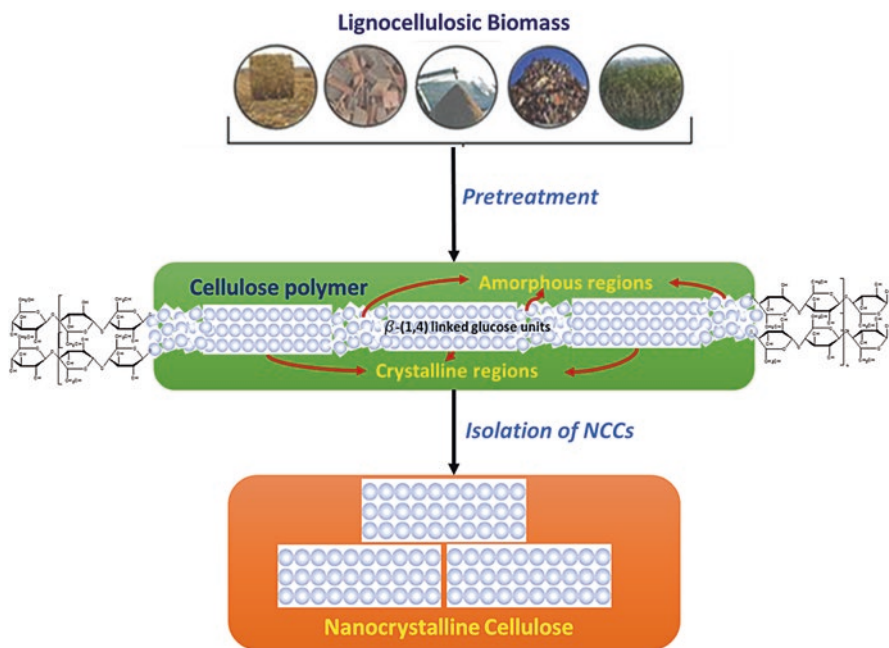


Fig. 17.1 Schematic representation of nanocrystalline cellulose production

17.2 Production of Nano-Crystalline Cellulose (NCC)

Traditionally, NCC can be isolated from any cellulose obtained from plants, animals, bacteria, and algae. However, due to high abundance of cellulose in wood and agricultural residues, these biomass sources have become major substrates for the extraction of NCC. Wood-based NCC extraction has also gained importance as these fibers are thinner than the bacterial cellulose (George and Sabapathi 2015). Abraham et al. (2011) have reported that pineapple leaf fiber produce fine NCC than banana and jute (Abraham et al. 2011). However, jute fiber is one of the cheapest materials to make the nanocellulose production cost-effective. Fortunati et al. (2012) have investigated the extraction of micro- and nanocellulose from okra fibers. Nonetheless, the production process of NCC is similar for all cellulosic materials (Fortunati et al. 2012). There are two stages involved in the isolation of NCC for any type of biomass.

First, the raw material is pretreated to separate cellulose from other constituents (lignin and hemicellulose of lignocellulose biomass). Second, the cellulose is treated to break the amorphous regions of the long glycosidic chain polymer. This is usually done by mechanical, chemical, and enzyme methods. Ranby (1951) reported the synthesis of cellulosic nanofibers for the first time using sulfuric acid. When cellulosic material is subjected to either mechanical or chemical treatments, the amorphous regions disintegrate and leave the crystalline regions intact in the form of short crystals. A number of industries are focusing on commercialization of different forms of NCC by evaluating various methods for economically feasible production (Antonio 2014).

17.3 Pretreatment of Biomass

There are different types of pretreatment techniques reported in literature that are used to separate biomass into two major streams, a solid stream containing cellulose and lignin and a liquid stream containing majorly hemicellulose (Dalli and Rakshit 2015). The pretreatment techniques can be categorized into thermal, chemical, or physical. In most cases, the pretreatment has to be optimized and controlled to avoid unwanted by-products. Some of the effective and most studied pretreatment techniques are reported here.

17.3.1 Hydrothermal Pretreatment

This is a widely used method to separate water soluble and insoluble polymers from the biomass (Ma et al. 2014). As the name indicates, water and heat are involved in this process. Mineral acids such as sulfuric acid are used to enhance the efficiency

of the process. Though this process is effective using mineral acids like H_2SO_4 , HCl , and H_3PO_4 (Hendriks and Zeeman 2009), waste disposal is a problem as the acid waste stream can cause environmental pollution. In order to avoid acid treatment, the process can be carried out under pressure (Saha et al. 2013). Hydrolysis does not occur below $100\text{ }^\circ\text{C}$ (Abatzoglou et al. 1992). Autohydrolysis, steam explosion, steam extrusion are some of the examples of hydrothermal treatment (Dalli and Rakshit 2015) which are considered to be useful depending on the type of biomass used.

17.3.2 Alkaline Hydrolysis

In the alkaline pretreatment process, biomass is treated with aqueous ammonia, sodium carbonate and hydroxides of sodium, calcium or potassium. Generally, lime and sodium hydroxide are used to hydrolyze the biomass at moderate temperature (Park and Kim 2012). Other types of alkaline treatments include the Ammonia Fiber Explosion (AFEX) and the Ammonia Recycling Percolation (ARP). Alkaline peroxide is another type of alkaline pretreatment where oxygen or hydrogen peroxide (1–3%) is added to biomass and catalyzed by the addition of lime or NaOH (Carvalho et al. 2008). These processes give better results by removing the lignin from the polysaccharides. In the AFEX process, liquid ammonia is added to biomass at a moderate temperature ranging from 40 to $140\text{ }^\circ\text{C}$ and under high pressure (250–300 psi) and the reaction is carried out for a shorter time (Teymouri et al. 2004; Keshwani and Cheng 2009). In the ARP process, ammonia is circulated through the biomass in a column reactor. This is more effective with hardwoods and corn stovers than in softwoods and results in high delignification and moderate hemicellulose solubilization of approximately 40–60% (Carvalho et al. 2008). In cases where most of the lignin and hemicellulose are separated, cellulose becomes the major component in the solid fraction.

17.3.3 Organosolvent Pretreatment

In this process, organic solvents (e.g. methanol, ethanol, ethylene glycol etc.) with or without acid catalysts (HCl , H_2SO_4) are used to extract most of the lignin from biomass. Organic solvents dissolve lignin in the presence of acid catalyst and some of the hemicellulosic sugar (Lee et al. 2014). If this pretreatment process is performed under high temperatures (185 – $210\text{ }^\circ\text{C}$), addition of acids is not necessary because deacetylation from the sugars make the medium acidic. However, when the acids are added externally, this process is more effective in solubilizing lignin and hemicellulose leaving solid cellulose residue, (Zhao et al. 2009). According to Lee et al. (2014), hydroxyl ions from the alcoholic solvents break the bonds of phenolic and polysaccharide linkages in lignin and hemicellulose to dissolve them.

This process has its benefits as it requires low energy to recover the components (Lee et al. 2014). However, it was also observed that organic solvents swell the cellulose fibers and reduce their crystallinity (McDonough 1993). Another demerit of this process is the formation of clumps of lignin while washing the pretreated biomass with water. Therefore, recovery of cellulose often becomes cumbersome and costly process.

17.3.4 Pretreatment Using Ionic Liquids

Pretreatment of lignocellulosics using ionic liquids is a relatively recent technique developed for isolating the cellulosic components from the lignocellulose matrix. Ionic liquids target the β -glycosidic bonds on cellulose polymer and make it soluble by hydrolyzing the linkages (Xiong et al. 2014). However, it is possible to control the concentration of ionic liquids to make cellulose and hemicellulose dissolve without disturbing the chain's structure (Lee et al. 2014). Ionic liquids are generally composed of an inorganic anion and an organic cation, which can be modified depending on the target compounds. Major benefit involved in this process is the recyclability of ionic liquids (Lee et al. 2014). Some examples of ionic liquids reported in literature are 1-alkyl-3-methylimidazolium [mim]⁺; 1-alkyl-2,3-dimethylimidazolium [mmim]⁺; 1-allyl-3-methylimidazolium [Amim]⁺; 1-allyl-2,3-dimethylimidazolium [Ammim]⁺; 1-butyl-3-methylpyridinium [C₄mPy]⁺; and tetrabutylphosphonium [Bu₄P]⁺ with n = number of carbons in the alkyl chain (Zavrel et al. 2009; Tadesse and Luque 2011; Lee et al. 2014). Ideally, ionic liquid should possess high dissolution capacity, low melting point, low viscosity, low toxicity and high stability. However, the drawback of using ionic liquids is the cellulose crystallinity would be reduced and become more amorphous. This is because of the tendency of ionic liquids to hydrolyze the hydrogen bonds in the cellulose polymer resulting in bond breaking and subsequent dissolution (Lee et al. 2014). The high costs of the ionic liquids are also an important factor that needs to be taken into account.

17.4 Isolation of Nanocrystalline Cellulose

Though the pretreatment techniques do not produce pure cellulose, most of the lignin and hemicellulose content need to be removed. The solid fraction obtained from the above pretreatment processes contains cellulose and some lignin. This material is then further treated to produce NCC. The purity, physical and mechanical properties of the product depend on the type of method used for the production. Some of the reported methods in literature are mentioned in Table 17.1 and described in detail as follows.

Table 17.1 Isolation methods and processes involved in NCC production

Treatment method	Processes	References
Mechanical	Milling, grinding, cutting, ultrasonication, microfluidization, cryocrushing	Ng et al. (2015), Marimuthu and Atmakuru (2015) and Frone et al. (2011)
Physical	Steam explosion	Cherian et al. (2010)
Chemical	Acid hydrolysis TEMPO-oxidation	Sacui et al. (2014) and Börjesson and Westman (2015)
Enzymatic	Exoglucanases: A and B type cellulases Endoglucanases: C and D type cellulases	George et al. (2011), Pääkkö et al. (2007), Lee et al. (2014) and Khalil et al. (2014)

17.4.1 Mechanical Processes

The mechanical process used for nanocrystalline cellulose production from the pretreated cellulose include milling, grinding, cutting, high pressure homogenization (steam explosion), ultrasonication, microfluidization, cryocrushing, etc. (Ng et al. 2015). The shear forces applied in mechanical treatment make the cellulose disintegrate and help in extracting the crystalline cellulose microfibrils in the form of a uniform powder (de Souza Lima et al. 2003). Common treatments like milling, cutting or grinding are done in Wiley mill or Fritish Pulverisette mills or grinding machines (Ng et al. 2015). Ribbon-like cellulose nanocrystals are usually obtained in this process. These fibers are then sieved in a vibratory sieve to separate fine particulate fibers. The pore size of the mesh used in the vibratory sieves is usually in the range of 50–250 μm . The smaller the size of the fine fibers, higher the activity in subsequent chemical treatments due to the higher availability of the active groups of cellulose to react with the chemical reagents (Ng et al. 2015). The finely ground fibers are washed with water to remove impurities and to make the fibers softer (Frone et al. 2011; Marimuthu and Atmakuru 2015; Ng et al. 2015). Rosa et al. (2012) suggested dewaxing the fibers in a solvent mixture of toluene/ethanol using a soxhlet type extraction (Rosa et al. 2012).

The other components of the lignocellulosic material, hemicellulose and lignin, often make the NCC fibers impure and reduce its crystallinity. Therefore, it is necessary to separate these materials from cellulose fibers. Commonly used techniques for purification include alkali bleaching treatment or mercerization using sodium hydroxide or potassium hydroxide, sodium chlorite, and acetic acid (Ng et al. 2015). Alkali solutions potentially dissolve the other components except cellulose fibers which can be easily filtered out (Acharya et al. 2011; Faruk et al. 2012). For most applications, the fiber concentration should be limited to the optimal range of 4–6% (w/w) during the alkali treatment because the low fiber to alkali ratio lead to chemical degradation, whereas high fiber to alkali ratio might result in inefficient modification by reducing the active sites of reaction (Ng et al. 2015).

17.4.2 *Ultrasonication*

It has been reported that ultrasonication processes enhance the efficiency of biomass acid hydrolysis (Brinchi et al. 2013). Production of NCC using ultrasonication in water or an organic acid has been reported in the literature (Filson et al. 2009). Although low yields were obtained, it has been proven that ultrasonication helps to increase the NCC yields. Ultrasonication is an advanced technique to isolate micro- and nanocellulose from lignocellulosic material. Ultrasonication associated grinding and homogenization is an effective and efficient method to produce NCC in large volumes (Hielscher Ultrasonics GMBH 2017). It was reported that oxidation of cotton linter pulp using 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)-NaBr-NaClO assisted with ultrasonication led to the production of carboxylated NCC (Qin et al. 2011). Leung et al. (2011) suggested a simple procedure to produce carboxylated NCC using ammonium persulfate instead of TEMPO, at 60 °C (Leung et al. 2011). This method showed relatively high yields of NCC and has the potential for scale up (Brinchi et al. 2013). However, this type of oxidation process is not efficient for the production of pure NCC. Besides producing low yields, use of TEMPO is relatively expensive and toxic to dispose. An advantage in this process is that the raw material can be used directly without any pretreatment steps for the isolation of cellulose.

17.4.3 *Chemical Treatment*

In the chemical treatment of lignocellulosics for NCC production, acid hydrolysis of cellulose is considered as an efficient method as it consumes less energy and produce rod-like crystal structures of cellulose nanofibers (Sacui et al. 2014). The strong acids easily disintegrate amorphous regions of the cellulose fibers, leaving the crystalline regions unaffected. However, boiling with strong sulfuric acid has its affect only up to a certain period, beyond which it slowly reduces the degree of polymerization of the polymer (George and Sabapathi 2015). The threshold level-off the degree of polymerization (LODP) varies with the type of biomass used to produce NCC. According to George and Sabapathi (2015), crystalline nanocellulose obtained from acid hydrolysis exhibit high polydispersity in molecular weight. This was assumed to be due to the lack of regular distribution of amorphous regions. Several other factors such as temperature, reaction time etc., also affect the quality of NCCs. In case of shorter reaction time is used, amorphous regions of the cellulose are retained in the solution and reduce the quality of the NCC. On the other hand, longer reaction time leads to depolymerization of cellulose crystals and reduces the aspect ratio of nanocrystals. The treatment of biomass at high temperature results in short chains of nanocellulose (Elazzouzi-Hafraoui et al. 2008). Bai et al. (2009) reported the synthesis of NCC whiskers from microcrystalline cellulose (MCC)

using sulfuric acid. They have reported that the relative centrifugal force (RCF) also affects the length of NCCs (Bai et al. 2009).

Use of other acids like HCl (Börjesson and Westman 2015), HBr, H₃PO₄ (Lee et al. 2009) to isolate NCCs from the cellulosic material have been reported in literature. A mixture of acetic acid and nitric acid was used to enhance the production of nanocellulose by Zhang et al. (2014). Aqueous solution of NCCs was synthesized using HCl by grafting technique. It has been reported that grafting on nanocrystals using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in a procedure known as oxidative carboxylation-amidation prevents the particle aggregation and induces the stability of the colloidal NCC solution.

17.4.4 Enzymatic Treatment

Cellulose treated with enzymes along with mechanical shearing and high pressure homogenization is a relatively new method being developed for NCCs production. Commercial cellulase enzyme is used in these methods to obtain NCCs with better physical properties. Enzymatic treatment is considered better than acid hydrolysis as less waste is produced after the process and its ecofriendly nature (George et al. 2011). Pääkkö et al. (2007) have developed a facile method for the usage of enzymes along with mechanical shearing. They reported that the incorporation of enzymatic hydrolysis reduced the energy consumption and has a drastic effect on the mechanical properties of the NCCs produced. Usually, the synergistic action of endoglucanases and exoglucanases or cellobiohydrolases on biomass leads to disintegration of cellulose at the solid-liquid interface (Lee et al. 2014). This results in a shorter chain length of nanocellulose fibers. Although, the enzymatic treatment provides high yields with high selectivity, the limiting factor is the cost of the enzymes. Cellulose degradation using these enzymes take longer time durations to produce the desired high yields of NCC. The slow rate of enzyme hydrolysis also eventually increases the cost of production.

17.5 Chemical Modifications of NCC

One of the important applications of NCC is its use in engineering products as composite material for reinforcement. The chemical modification of nanocellulose is very helpful in improving the physical properties of polymer matrix in biocomposites (Börjesson and Westman 2015). Some of the chemical modification methods along with the functional agents used are listed in the Table 17.2.

Strengthening of nanocellulose-reinforced composites can be done by modifying the NCCs using peroxide. The hydroxyl groups on glucose molecules in a nanocellulose chain are of great interest to synthetic chemists as they can be modified modify to produce NCCs with different properties. Usually, chemical modification

Table 17.2 Chemical modification methods of NCC using various functional agents

Methods	Mechanism	Functional agents	References
Oxidation	Conversion of the hydroxyl groups of cellulose backbone	Maleic acid, lignin, polyvinyl alcohol, polyvinyl acetate	Börjesson and Westman (2015)
Coupling	Formation of covalent bonds between the hydroxyl groups and coupling agents	Organofunctional silanes, polypropylene etc.	Majeed et al. (2013)
Acetylation	Addition of acetyl group on the nanocellulose surface	Acetic acid, propionic acid, alkenyl succinic anhydride (ASA), acetic anhydride and acetyl chloride	Panaitescu et al. (2013) and Majeed et al. (2013)
Grafting	Transforming nanocellulose into a long aliphatic chains	Polycaprolactone, polyurethane, thermos-responsive polymers	Rebouillat and Pla (2013) and Dufresne (2010)

is done to improve the interface between two incompatible phases (Ng et al. 2015). Various compatibilizing agents such as maleic acid (Majeed et al. 2013), lignin, polyvinyl alcohol, polyvinyl acetate have been studied in literature (Ng et al. 2015) to strengthen the polymer containing NCCs. Lignin treatment includes the coating of nanocellulose with kraft lignin which exhibited the compatibility with both hydrophobic and hydrophilic matrices in a composite (Alemdar and Sain 2008). The use of these agents can enhance the interfacial adhesion between nanocrystalline cellulose and the polymer matrix.

Chemical modifications on the surface of NCC can be done by the formation of covalent bonds with the hydroxyl groups on glucose molecules. Several coupling agents have been studied to induce the covalent bonding in the nanocellulose and composite matrix (Majeed et al. 2013). Esterification is beneficial as it requires no solvent and is highly efficient in the conversion of hydroxyl groups and does not affect the crystalline structure of nanocellulose (Ng et al. 2015). The functional properties of the surface of nanocellulose can be altered by esterification. The polar hydroxyl groups are replaced by non-polar carbonyl groups (Panaitescu et al. 2013) which results in altered characteristics.

Acetylation of nanocellulose also one of the commonly employed method to modify the properties of NCC. Acetic acid, propionic acid, alkenyl succinic anhydride (ASA), acetic anhydride and acetyl chloride have been reported as major carriers of acetyl groups which can be easily transferred on to the nanocellulose surface (Majeed et al. 2013; Panaitescu et al. 2013). Dufresne (2010) has reported the studies on a novel modification of nanocellulose by transforming it into a long aliphatic chain. Two approaches such as “grafting-onto” and grafting-from” were used to graft the polymer onto the surface of NCC. In both the approaches, the nanocellulose was suspended in the solvent during grafting (Rebouillat and Pla 2013). In the “grafting-onto” approach, a previously synthesized polymer is directly attached to the available hydroxyl groups on the NCC chain using a coupling agent (e.g. isocyanate or peptide) (Ng et al. 2015). The polymers involved in this type of

modification are poly-caprolactone, polyurethane, thermos-responsive polymers etc. (Rebouillat and Pla 2013). The advantage of such methods is that the polymers can be fully characterized before attaching to the NCC chain. However, the reaction time was found to be too long for such modification due to the steric hindrance from the polymer molecules (Rebouillat and Pla 2013).

On the other hand, “grafting-from” is useful as it helps in obtaining long chains of polymers. Unlike grafting-onto, the polymers are built on the surface of the NCC using immobilized initiators via the atom transfer radical polymerization (ATRP) (Rebouillat and Pla 2013). The major bottleneck of this method is that the polymer cannot be characterized before the grafting method. However, the useful factors in this type of surface grafting are the high reaction rates, production of no by-products and high chemical stability (Espino-Perez et al. 2013).

Extensive research is taking place to alter the functional properties of the nanocellulose by reacting it with various reagents having derivative functional groups. Recent reports in literature indicate rapid advancement in improving binding ability and hydrophilicity of NCC (Ng et al. 2015). However, some of the upstream processes for the production of NCCs consume high amount of energy. Some of the recent studies on the energy consumption are discussed below.

17.6 Energy Consumption in Preparing NCC

The energy consumption for NCC production depends mainly on the source of cellulosic fibers and the isolation processes. Different mechanical methods are used to isolate the nanofibrillated cellulose including high pressure homogenization, microfluidization, grinding, cryocrushing and high intensity ultrasonication (Khalil et al. 2014). However, one of the main challenges of all these approaches in nanocellulose production and application results in high energy consumption. Increasing applications of nanocellulose in various field including biomedical uses, food packaging, coating and etc. (George and Sabapathi 2015) requires energy-efficient approaches its production in an industrial scale. There are only a few studies available on energy consumption for a specific pretreatment or property. Further investigation on nanocellulose preparation, modification, production and developing economical approaches are necessary before it can be applied successfully in a large scale.

Production of microfibrillated cellulose is one of the main steps in the NCC isolation. It was reported that, over 25,000 kWh per ton is required for the production of microfibrillated cellulose (MFC) as a result of the multiple passes through the homogenizers (Klemm et al. 2011).

Pretreatments are reported to reduce the energy consumption from 20,000 to 30,000 kWh/ton to 1000 kWh/ton for cellulosic fibers, while improving the production conditions and fiber swelling properties (Zhu et al. 2011). Mechanical and chemical pretreatments are regarded as effective approaches which significantly reduce energy consumption (Stelte and Sanadi 2009). As an example, TEMPO-mediated oxidation of cellulose fibers achieved some level of success in efficiently producing

NFC (Saito et al. 2007). Further, it is reported that enzymatic treatment (Henriksson et al. 2007; Janardhnan and Sain 2007) of cellulose prior to the defibrillation facilitate disintegration requires lower energy for producing MFC. Ankerfors (2012) studied three alternative processes for producing microfibrillated cellulose in which pulp fibers were first pretreated and then homogenized. In the first process sulfite pulp were put through two refining steps and an enzymatic pretreatment. Then high pressure (1600 bar) homogenization with 8 passes was used. 33 and 90 kWh/ton pulp was measured for the first and second refining stage and the total energy required was calculated to be 2344 kWh/ton. The paper claimed 91% reduction in energy use, as the energy consumption reported earlier was 27,000 kWh/ton without pretreatments (Klemm et al. 2011). In the second process, chemical pretreatment such carboxymethylation was applied prior to high pressure (1650 bar) homogenizing. Mechanical energy consumption was calculated to be 2221 kWh/ton in this way. The third process associated with combined enzymatic and mechanical pretreatment to facilitate disintegration. Approximately the same amount of energy as in the second process was calculated. It was reported that reduction of required energy to 500 and 1500 kWh/ton for the second and the third process respectively can be obtained by optimization of the parameters of reaction and treatment such as concentration and pressure. In terms of low energy consumption, it is reported that these three processes have the potential for industrial scale production.

An overall assumption is that MFC can be produced with an energy consumption of 500–2300 kWh/ton by these methods. Also, the characterizations of the produced materials have been investigated in different ways and it has been demonstrated that the produced MFC fibrils were approximately 5–30 nm wide and up to several microns long. The number of homogenization steps does matter as well. Even though an increased number of steps are found to improve the quality of the product, each homogenization step costs 2200 kWh/ton. Therefore, the nanocellulose isolation process conditions should be taking into this account (Ankerfors 2012).

Another study by Spence et al. (2011), studied the effect of processing on microfibril and film properties, relative to energy consumption on bleached and unbleached hardwood pulp samples by homogenization, microfluidization, and micro-grinding. Film densities of samples in all three approaches were reported approximately to be 900 kg/m³. However, higher toughness values were reported for microfluidization and micro-grinding with less required energy compare to homogenization.

In fibers processing energy consumption per pass was 3940 kJ/kg by homogenizer and the 620 kJ/kg by micro-grinder. The microfluidizer energy measurements was 200 kJ/kg with operating pressure of 69 MPa, 390 kJ/kg under 138 MPa pressure, and 630 kJ/kg with 207 MPa.

Energy is highly influenced by parameters such as number of passes and flow rate in each processing methods. Homogenization, for instance, had a much slower processing flow rate than the microfluidizer and the micro-grinder, which notably increased the amount of required energy. The processing rates of the suspension were 2 kg/min for micro-grinding, 1 kg/min for microfluidization, and 0.2 kg/min for homogenization. Higher pressures of the microfluidizer also raise the energy required. Generally, the total energy of approximate 9180 kJ/kg for the microfluidizer with

pretreatment, 9090 kJ/kg for the grinder with pretreatment, and 5580 kJ/kg for the grinder without pretreatment and 31,520 kJ/kg for the homogenizer is required in processing of MFC films with maximum accessible properties (Table 17.3).

Studies have showed marked increase in tensile index of the MFCs from bleached hardwood fiber after microfluidization and micro-grinding, while homogenization was not considered as an energy-efficient process. However, processing of the unbleached hardwood fibers was more efficient. With overall lower energy consumption, microfluidizer process leads to the highest tensile index (Spence et al. 2011).

From a review of literature, it seems that the following assumptions can be useful for optimizing the processes. Firstly, in microfluidization, even though the increased pressure leads to significant increase in the energy consumption, toughness and tensile index decreases as a result of the microfibrils damage at such high temperature. Secondly, increasing the number of passes would increase the energy consumption, with only a small improvement in properties. It is recommended that 5 steps should be the maximum number of passes in microfluidizing. In terms of tensile strength and toughness, maximum 8 passes are suggested in homogenization including pretreatment (Shahbaz and Lean 2012).

Furthermore, similarity of tensile properties of pretreated and non-pretreated samples shows that no pretreatment is required for micro-grinder processing which leads to great reduction in energy consumption. In general, among the three methods including homogenizer, microfluidization and micro-grinding, nano or micro crystalline cellulose with superior mechanical, optical and physical properties and less energy consumption are produced through microfluidization with a refining pretreatment and the micro-grinding of wood fibers. Finally, unless energy consumption is reduced sufficiently, NCC use at an industrial scale will be limited to some high value applications.

17.7 Applications of Nanocrystalline Cellulose

Celluloses are biocompatible, nontoxic and stable in nature. Even though nanocrystalline cellulose (NCC) are nanometers in dimension, the innate properties of cellulose are retained. Besides the cellulosic characteristics, they possess some unique optical and

Table 17.3 Comparison of energy consumption for homogenization, microfluidization, and microgrinding during NCC production

Methods	Rate flow (kg/min)	Required energy per pass (kJ/kg)	Total energy required (kJ/kg)
Homogenization	0.2	3940	31,520 (with pretreatment)
Microgrinding	2	620	9090 (with pretreatment) 5580 (without pretreatment)
Microfluidization	1	200/69 MPa 390/138 MPa 630/207 MPa	9180 (with pretreatment)

mechanical properties. Furthermore, nanocrystalline cellulose possess high surface area, better rheological properties, crystallinity, alignment and orientation, etc. Due to these characteristics nanocrystalline cellulose has potential applications in different sectors such as health care, food and beverages, cosmetics, electronics, etc. Its use as a reinforcing agent for nanocomposite materials (Lin and Dufresne 2014) and in the areas of nanomedicine (Dufresne 2013) has been extensively studied.

17.7.1 Use of Nanocomposite Films Production

One of the major applications of NCC is its use as a reinforcing material (or as a filler) during the production of nanocomposite materials such as nanocomposite films. Polymer nanocomposites are multiphasic material made up of polymer and nanomaterials (Jeon and Baek 2010; George and Sabapathi 2015). Because of their nanometric size and large surface area (due to smaller size of the reinforcing materials), they exhibit unique properties. Nanocomposite films obtained using NCC possess characteristics such as low permeability to moisture, gases, aroma, and oil. Due to this, they are commonly used for packaging in food and biomedical field (George and Sabapathi 2015). The properties of nanocomposite films mainly depend on two factors (1) morphology and dimensions of NCC and polymeric matrix and (2) processing method applied. Geometric aspect ratio is one of the factors that dictates the mechanical properties of nanocomposites (Peng et al. 2011). It is defined as the length to diameter (L/d) of the fillers used. Aspect ratio in turn depends on the types of cellulose fibers used and the production conditions involved. Since NCCs have high aspect ratio, they are considered to provide best reinforcing effects (Peng et al. 2011; Dufresne 2013; George and Sabapathi 2015). Good dispersibility of nanocrystals in the polymer matrices are required to enhance the mechanical properties of nanocomposite material. Since, NCCs disperse well on hydrophilic system, they are best suited for water dispersible polymers such as latexes (Hubbe et al. 2008). However, NCCs can also be modified to improve their dispersibility in hydrophobic systems (George and Sabapathi 2015). Thus, some of the commonly used processing methods to produce nanocomposite films includes casting evaporation, electrospinning, extrusion, and impregnation, monolayer films, and multilayer films (Peng et al. 2011).

17.7.2 Biomedical Applications

Due to the safe and natural form of nanocrystalline cellulose, it is gaining increasing attention in biomedical applications. Different scientists have explored its use for the production of biomedical materials suitable for practical clinical applications (Lin and Dufresne 2014). Some of the possible uses of NCCs in biomedical applications have been discussed below.

17.7.2.1 Carrier for Drug Delivery

Toxicity assessment of NCC on human cell lines, insect cells, and aquatic species has been done by various authors (Roman et al. 2009; Kovacs et al. 2010; Male et al. 2012). Most of the results obtained in these studies showed that NCCs were non-toxic to all the samples studied. This makes NCC a potential carrier in targeted drug delivery systems. On the one hand, use of NCC as an excipient in pharmaceutical industries holds considerable potential due to reduced size, hydrophilic nature, and biocompatibility. On the other, with the use of NCC as a carrier for drug delivery, optimal control of dosing can be obtained and large amounts of drugs can be bound to its surface. This is due to its large surface area and possibility of acquiring negative charge during hydrolysis. Surface modification of NCC can also be done to bind nonionized and hydrophobic drugs which normally do not bind to cellulose and its derivatives (George and Sabapathi 2015; Taheri and Mohammadi 2015).

Common forms of nanocellulose-based drug carriers include microspheres (or microparticles), hydrogels (or gels), and membranes (or films) (Lin and Dufresne 2014). Shi et al. (2003) examined the morphology of drug nanoparticles coated onto the cellulosic beads. Similarly, incorporation of the NCC particles into hydrogels has the potential of using such nanocomposite hydrogels as a controlled drug delivery vehicle (Zhang et al. 2010). Some studies carried out by (Clift et al. 2011) have shown that cellulose nanocrystals may slightly induce some dose-dependent cytotoxic and inflammatory effects on human lung cells. Thus, further studies on risk assessment of NCC however should be done before its application in drug delivery system (Peng et al. 2011; Lin and Dufresne 2014).

17.7.2.2 Bioimaging and Biosensor

Nanocellulose can be a very useful material for use in biosensor technologies. It possesses biocompatible transducer surfaces which makes it useful in sensor applications (Edwards et al. 2013). NCC can be derivatized at the hydroxyl regions to make it covalently bound to bioactive molecules. They have chiral neumatic structures which are characteristic for sensitive optical properties (Shopsowitz et al. 2010). Different types of nanocellulose such as nanocomposites, surface grafted molds, and microdialysis membranes were found to show excellent properties at bio-interface of a probe (Edwards et al. 2013). It was reported that cellulose can be used as stimuli responsive mediators by modifying it through radical polymerization (Kang et al. 2013). Such modified celluloses can be used in drug delivery and for bioimaging application (Dong and Roman 2007). These authors reported a method to label NCC with fluorescein-5'-isothiocyanate (FITC). The interaction between labeled NCC with cells where then evaluated using fluorescence techniques.

NCC can be used in biosensing by conjugated it with different biological moieties (such as nucleic acids) or metallic nanoparticles (Lam et al. 2012). Moss et al. (1981) reported a method for producing a DNA-cellulose hybrid suitable for purifying complementary mRNA from total poly(A)-enriched RNA by affinity chromatography.

NCC can also be used to produce robust, porous electrodes and sensors. It can be used to replace the cellulose which has been combined with TiO₂ nanoparticles (Pang et al. 2016) and chitosan for their potential use as biosensors (Manan et al. 2016).

17.7.3 Enzyme Immobilization

NCC has large surface area and is non-porous in nature which makes it suitable for immobilizing proteins or enzymes (Lam et al. 2012). Yang et al. (2008) reported a model system to remove chlorinated phenolic compounds in aqueous solution by immobilizing peroxidase onto NCC. The obtained immobilized peroxidase showed improved activity compared to its soluble counterpart. The immobilized samples had enzyme activity 594 U/g and stable for 3 months at 5 °C. Furthermore, NCC functionalized with gold nanoparticles has been characterized as a support for immobilization of enzymes (Mahmoud et al. 2009; Lam et al. 2012). For instance, cyclodextrin glycosyl transferase (CGTase) and alcohol oxidase can be immobilized on NCC with high enzyme loading capacity. Activity yield and CGTase loading of 70% and 165 mg/g were, respectively, obtained when such NCC was used as matrices for immobilization. This value is higher than those obtained with other commonly used matrices (Ivanova 2010). Recently, detection of phenol using tyrosinase immobilized in the NCC/Chitosan nanomaterial film has been reported (Manan et al. 2016).

17.7.4 Antimicrobial Application

Use of NCC for antimicrobial applications has been demonstrated by Drogat et al. (2011). The author reported the method used to produce silver colloidal suspension using NCC. The obtained Ag-NCC solutions showed inhibiting activities against *E. coli* and *S. aureus*. The inhibiting effect was attributed to the interaction of NCC with the bacterial cell wall. Such Ag nanoparticle NCC suspensions have the potential to be used in antiseptic solutions or wound healing gels. However, detail study involving the long-term toxicity of Ag nanoparticles is yet to be done (Lam et al. 2012). This will confirm the expectations of the possible use of NCC as antimicrobial agents.

17.7.5 Other Applications

In addition to aforementioned applications, use of NCCs as iridescent pigments and biomolecular NMR contrast agent has also been explored (Fleming et al. 2001; Peng et al. 2011). Its use as a reinforcing agent for the production of low thickness polymer electrolytes used in lithium battery has also been reported by some authors

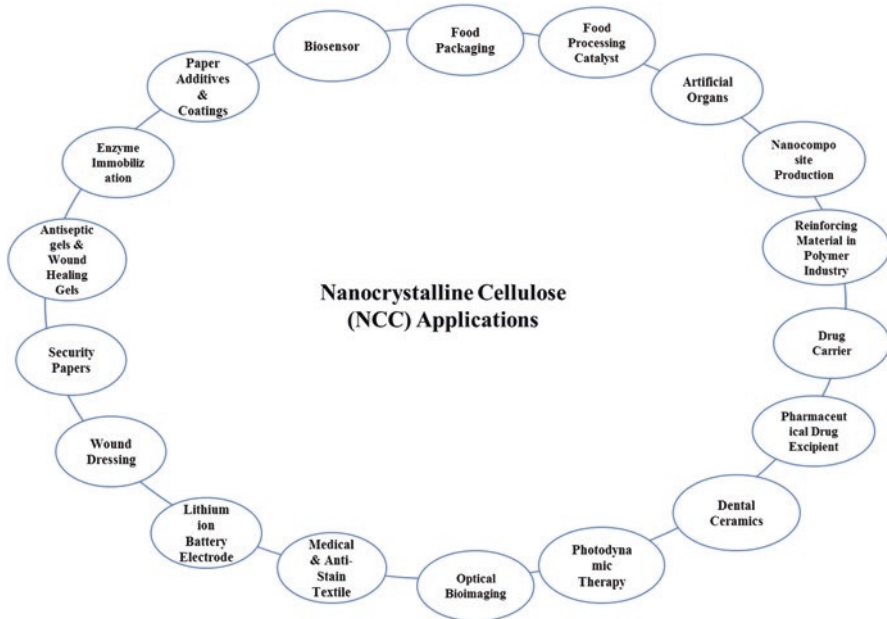


Fig. 17.2 Application of nanocrystalline cellulose in various sectors

(Schroers et al. 2004; Samir et al. 2005). Due to improved crystallinity and interfacial interaction, incorporation of NCCs in polymer nanocomposites can improve the mechanical performance, thermal stability, and optical properties of the same. Thus, biodegradable nanocomposite films with lower permeability to moisture, gases, aromas, and oil can be produced by inclusion of nanocrystalline cellulose. Such obtained films have numerous application in food and biomedical packaging areas (George and Sabapathi 2015). NCCs are biocompatible and their mechanical properties are like natural tissues. Thus, studies involving the use of NCCs as a scaffolding to grow tissue have also been carried out. The use of NCC is being studied in many areas as detailed here. The possible applications of nanocrystalline cellulose in different areas have also been depicted in Fig. 17.2.

17.8 Limitations of NCC Usage

Though NCC was found to be a potential material for several applications, it has several limitations in its upstream processing. For instance, oxidizing the cellulose make the amorphous fibers in NCCs disperse in the aqueous suspension of crystalline cellulose. Separation of these fine fibers is a major hurdle in producing pure NCC. Its usage is limited by factors like its hydrophobic nature and water swelling characteristics in the amorphous regions (Hubbe et al. 2008). Using high

concentration sulfuric acid 63.5% (w/w) to produce NCC (Bondeson et al. 2006) also has a major drawback in the perspective of environmental aspects. Despite the use severe conditions, NCC yields have been found to be low (20–40%) (Bondeson et al. 2006; Hamad and Hu 2010). An efficient and reliable process is necessary to maintain the uniform size, aspect ratio, and surface chemistry. It should provide more control in NCC suspensions (Brinchi et al. 2013). Therefore, standardization of the process is necessary to obtain fine NCC fibers. Technological advancements are necessary to develop a method to produce nanocellulose with controlled size, length, and surface properties at low costs. Drying of NCC is necessary to produce in its powder form. It was not listed as one of the limitations by many of the literature reports. However, the conventional drying methods like centrifugation and high temperatures have significant effect on NCC and induce agglomeration (Brinchi et al. 2013). According to Lu and Hsieh (2012), freeze drying and supercritical drying produced a matrix of agglomerates with various sizes of nanocellulose. Therefore, it is important to develop an efficient drying method to produce NCC without altering its structural or functional properties. A number of research studies indicated that the costs and commercial scale production are also the major drawbacks in the production of NCC (Brinchi et al. 2013). However, with the amount of research ongoing on the production, modification, and application of NCC, one can be optimistic about its use in a number of ways in the near future.

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