# Chapter 8
# Nano-Based Materials and Their Synthesis

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## 8.1 Introduction

In recent years, a new promising research area – nanotechnology – has a great deal of interest in various fields. Nanoparticles (NPs) are particulates characterized as scatterings of strong particles with not less than one measurement of 10–1000 nm in size. The surface region is the main vital element of NPs to volume proportion, permitting corporation with different particles. However, it specifically implies the precise manipulation of molecules and atoms in order to design and control of properties of the nanomaterial. Recently, in a couple of years, nanotechnology has attracted an extraordinary interest due to its potential effects on various logical ranges, for example, pharmaceutical industries, space and hardware businesses, etc. Innovation of nanoparticles allows little estimated materials and structures in the scope of couple of nanometers to fewer than 100 nm. Nanoparticles with the same synthetic organization show extensively changed substance, organic and physical properties, in view of their high surface-to-volume extent. Recently these particles have been used in different fields of drug transport, hyperthermia of tumors, antimicrobial activities etc. (Fig. 8.1). A key domain of examination in nanotechnology discusses about the combination of nanometer ranging particles of diverse sizes, shapes, and monodispersity. Therefore, development of environmental-friendly and cost-effective synthesis of nanoparticles is a crucial task. There are different

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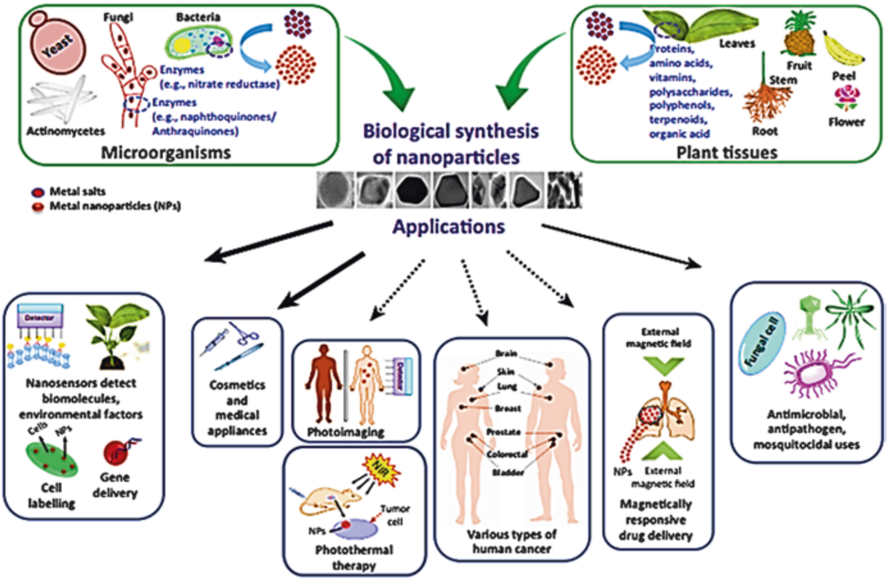

**Fig. 8.1** Application of nanoparticle in various systems

microorganisms possessing the ability to synthesize nanoparticles, having the ability to be modified and exploited to fulfill the purpose. The metallic nanoparticles are becoming increasingly important due to their potential application in many fields. Thus using nanotechnology may extend service life, limit the potential for environmental damage, and reduce failure rates. The present chapter focuses on providing an overview and a discussion of metallic nanoparticle synthesis by various biological and non-biological ways. Therefore, a green, nontoxic way of synthesizing metallic nanoparticles is needed in order to allow them to be used in a wider range of industries. This could potentially be achieved by using biological methods. This review will focus on how material science and biology can work together to create a green way of synthesizing metal nanoparticles for a wide range of uses.

## 8.2 Green Synthesis of MNPs (Biological/Bioreduction)

Much literature has been reported till date on the biological synthesis of MNPs using microbes, i.e., bacteria and fungi, and plants, because of their antioxidant/reducing properties typically responsible for reduction of metallic compounds to their respective MNPs (Fig. 8.2). Since the early 19th century, plant extracts have been known to have the ability to reduce MNPs, but the mechanism involved was not well understood. Recently, in medical science, MNPs synthesized using green technology have attracted a great deal of interest. Magnetic nanoparticles synthesized using green technologies over chemical-based methods have several advantages, i.e., more eco-friendly, easily scaled up, cost-effective, and comparatively require

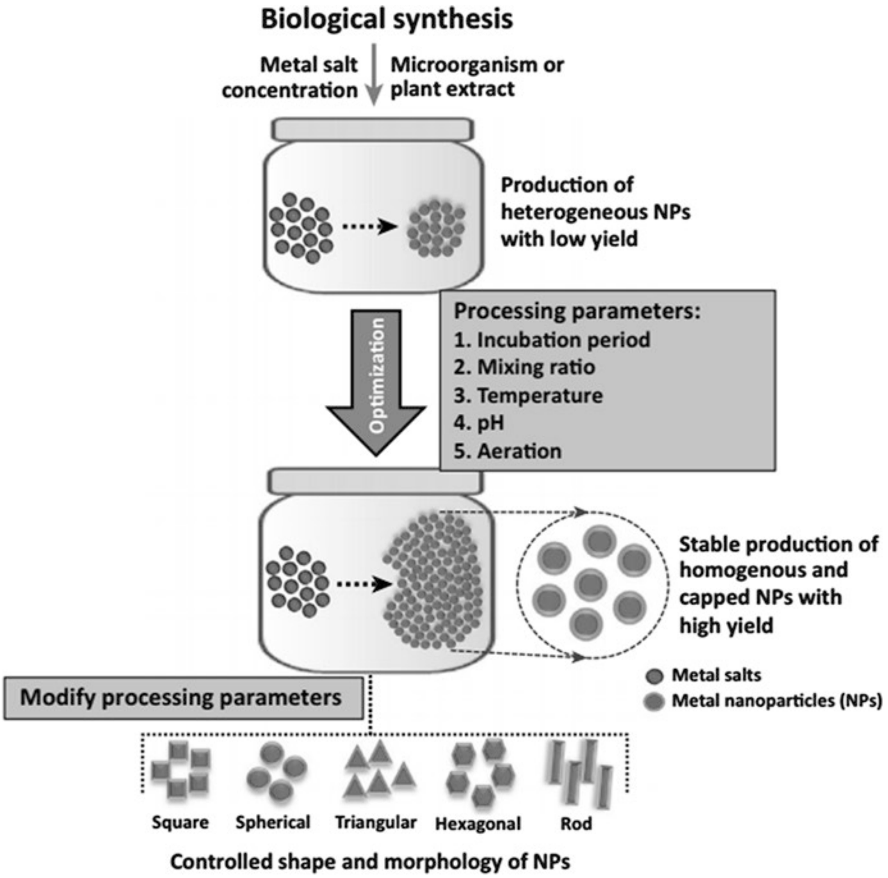

**Fig. 8.2** Parameters for producing biological nanoparticles

less energy, pressure, temperature, and other toxic chemicals. In the synthesis of MNPs, plant extracts may act as both stabilizing and reducing agents which directly influence the characteristics of nanoparticles (NPs). Different plant extracts contain different phytoconstituents like catechins, flavonoids, polyphenols, enzymes, alkaloids, vitamins, and functional groups, i.e., plant pigments, polysaccharide, tannins, which are responsible for bioreduction process of metal salts to MNPs. Bioreduction process typically involves simple mixing of aqueous extract with aqueous metallic salt solution, and reaction is carried out at room temperature. The biological synthesis of MNPs involves microorganisms and is considered as bottom-up approach. In this process nanoparticle formation occurs due to oxidation of metal ions occurs in presence of biomolecules i.e. sugars, enzymes, proteins secreted by microorganisms. However, the complete mechanism for synthesis of metallic nanoparticles is not well explored due to the fact that a different microorganism interacts differently with metal ions. Thus the formation of nanoparticles by biochemical processing, environmental factors, and its interaction ultimately determine the formation, size, and morphology of the nanoparticle.

## 8.3 Green Synthesis of Metallic Nanoparticles Using Plant Extracts

The use of different parts of plant or plant extracts for synthesis of silver nanoparticles has drawn attention, due to its economical, rapid, eco-friendly, non-pathogenic, and a single step technique for the biosynthesis processes. The stabilization and reduction of silver metal ions by combination of biomolecules of plant extract, i.e., saponins, proteins, polysaccharides, amino acids, phenolics, enzymes, vitamins, tannins, terpenoids, and alkaloids, are already established to have medicinal values and are environmentally benign.

Various plant extracts are reported to facilitate synthesis of nanoparticles, as mentioned in Table 8.1. Various MNP types (of different metals) were achieved using GS methodology. This is an indication of high reducing potentials of plant phytochemicals that neutralize uni- or multivalent metallic cations ($Mn^+$) into neutral atoms ($M^o$) for MNP synthesis. This might be due to the failure of the plant biomolecules to reduce metal cations with lower reduction potentials. Thus screening of plant biomolecules having high electron-donating capacity can be one of the efficient options for making GS a common modality of MNP synthesis. The innumerable angiospermic plant species are being used as remedies for diseases and also as a part of our diet. Therefore, during plant selection, important technical aspects, such as availability, socioeconomic importance, edibility, ethnobotanical background apart from the reducing nature of selected plant species. Randomized selection procedure might result in MNP synthesis, but biocompatibility issue may put it in a nonprogressive research interest. Angiospermic plant species, such as *Centella asiatica, Azadirachta indica, Camellia sinensis, and Aloe vera*, are the frontline examples of plant species that have been highly explored for their medicinal values and also have clinical relevancy (Table 8.1).

## 8.4 Nanoparticle Synthesis Using Microorganisms

Microorganisms are the main nanofactories that hold massive, eco-friendly, and cost-effective tools, which avoid toxic, harsh chemicals and decrease high energy demand required during physiochemical synthesis. Microorganisms have the capability to accumulate and detoxify heavy metal potential due to several enzymatic action and reaction, which reduces metallic salts to metallic nanoparticles (MNPs) with a narrow range of size distribution with less polydispersity. The mechanism and experimental methods of synthesizing nanoparticles in microorganisms. Over the past decades, microorganisms, such as bacteria, fungi, and yeasts, have been used

**Table 8.1** Plant species used for green synthesis of different metallic nanoparticles (MNPs)

| Plant species | Plant material | Type of MNPs | Mechanism/causative agent | Size of MNPs (nm) | References |
|---|---|---|---|---|---|
| *Azadirachta indica* | Kernel | Au, Ag | Azadirachtin | 50–100 | Shukla et al. (2012) |
| *Camellia sinensis* | Leaves | Au | Catechins | 15–42 | Nune et al. (2009) |
| *Jatropha curcas* | Latex | Pb | Curcacycline A and B | 10–12 | Joglekar et al. (2011) |
| *Geranium* | Leaves | Ag | Terpenoids (not specified) | 16–40 | Shankar et al. (2003a) |
| *Nelumbo nucifera* | Leaves | Ag | Not mentioned | 25–80 | Santhoshkumar et al. (2011) |
| *Lemongrass plant extract* | Leaves | Au | Sugar derivative molecules | 200–500 | Shankar et al. (2005) |
| *Avena sativa* | Stems | Au | Not specified | 5–85 | Armendariz et al. (2004) |
| *Aloe vera* | Leaves | Ag | Not specified | 70 | Medda et al. (2015) |
| *Cinnamomum camphora* | Leaves | Ag | Polyol compounds | 64.8 | Huang et al. (2007) |
| *Syzygium aromaticum* | Flower buds | Cu | Eugenol | 5–40 | Subhankari and Nayak (2013) |
| *Euphorbia esula* | Leaves | Cu | Flavonoids and phenolic acids | 20–110 | Nasrollahzadeh et al. (2014) |
| *Camellia sinensis* | Leaves | $Fe_2O_3$ | Polyphenols | 5–15 | Hoag et al. (2009) |
| *Eucalyptus* | Leaves | $Fe_2O_3$ | Epicatechin and quercetin glucuronide | 20–80 | Wang et al. (2014) |
| *Aloe barbadensis miller* | Leaves | ZnO | Phenolic compounds, terpenoids | 25–40 | Sangeetha et al. (2011) |
| *Nephelium lappaceum* L. | Peels | MgO | Not mentioned | 100 | Suresh et al. (2014) |
| *Nephelium lappaceum* L. | Peels | NiO | Nickel-ellagate complex formation | 50 | Yuvakkumar et al. (2014) |
| *Clitoria ternatea* | Whole plant | MgO | Bioactive compounds | 50–400 | Sushma et al. (2016) |
| *Cintella asiatica* | Leaves | Au | Phenolic compounds | 9.3 and 11.4 | Das et al. (2010) |
| *Camellia sinensis* | Leaves | Pt | Pure tea polyphenol | 30–60 | Alshatwi et al. (2015) |
| *Asparagus racemosus* | Tuber cortex | Pd | Bioactive compounds | 1–6 | Raut et al. (2013) |

to synthesized extra- and intracellular MNPs given in Table 8.2. A biological procedure for MNP synthesis has been informed using bacterial biomass, supernatant, and derived constituents. Among the several methodologies, extracellular synthesis of MNPs has received much attention because it removes the downstream processing process which is required for the recovery of MNPs in intracellular methodologies. Moreover, metal-resistant genes, proteins, enzymes, cofactors, and organic substance

**Table 8.2** Microbial synthesis of different metallic nanoparticles (MNPs)

| Bacteria | Nanoparticle | Size | Morphology | References |
|---|---|---|---|---|
| **Bacterial** | | | | |
| *Aeromonas* sp. | Ag | 6.4 | Spherical | Rai et al. (2009) |
| *Bacillus megaterium* | Au | 1.9 | Spherical | Sanpo et al. (2013) |
| *Escherichia coli* (DH5?) | Au, Ag | 10–50 | Spherical, triangular | Mahanty et al. (2013) |
| *Klebsiella (aerogenes, pneumoniae)* | CdS, Ag | ~52 | Spherical | Shahverdi et al. (2007) |
| *Nocardiopsis* sp. MBRC-1 | Ag | 45 | Spherical | Manivasagan et al. (2013) |
| *Shewanella* | Au, $Fe_3O_4$ | | | Konishi et al. (2006) |
| *Thermoanaerobacter ethanolicusTOR-39* | Co, Cr Ni and $Fe_3O_4$ | 5–25 | Octahedral | Rai et al. (2008) |
| *Pseudomonas stutzeri* AG259 | Ag, $Ag_2S$ | 20–50 | Nanocrystal | Joerger et al. (2000) |
| *Lactobacillus* sp. | Au, Ag, Au-Ag | 50 | Hexagonal/counter | Nair and Pradeep (2002) |
| *Desulfovibrio desulfuricans* | Pd | 10–15 | | Yong et al. (2002) |
| *Corynebacterium* sp. SH09 | Ag | 0.3–30 | | Zhang et al. (2005) |
| *Lactobacillus* sp. | Ti | | Spherical | Prasad et al. (2007) |
| *Shewanella oneidensis* | $Fe_3O_4$ | 40–50 | Rectangular, hexagonal | Perez-Gonzalez et al. (2010) |
| *Yeast cells* | $Fe_3O_4$ | | Wormhole-like | Zhou et al. (2009) |
| *Saccharomyces cerevisiae* | $Sb_2O_3$ | 2–10 | Spherical | Jha et al. (2009) |
| *Lactobacillus* sp. | $BaTiO_3$ | 20–80 | Tetragonal | Jha and Prasad (2010) |
| *Fusarium oxysporum* | $TiO_2$ | 6–13 | Spherical | Bansal et al. (2005) |
| *Fusarium oxysporum* | $ZrO_2$ | 3–11 | Spherical | Bansal et al. (2004) |
| **Fungus** | | | | |
| *Fusarium oxysporum* | Au | 20–40 | Spherical, triangular | Mukherjee et al. (2002) |
| *F. oxysporum* | Zr | 3–11 | Quasi-spherical | Bansal et al. (2004) |
| *F. oxysporum* | Au-Ag | 8–14 | | Senapati et al. (2005) |
| *F. oxysporum* | Si | 5–15 | Quasi-spherical | Bansal et al. (2005) |
| *F. oxysporum* | Pt | 10–50 | Triangle, hexagons, square, rectangles | Riddin et al. (2006) |

(continued)

**Table 8.2** (continued)

| Bacteria | Nanoparticle | Size | Morphology | References |
|---|---|---|---|---|
| *F. oxysporum* | $BaTiO_3$ | 4 | | Bansal et al. (2006) |
| *V. luteoalbum* | Au | 10 | Spherical | Gericke and Pinches (2006) |
| *Aspergillus flavus* | Ag | 8.9 | | Vigneshwaran et al. (2007) |
| *Coriolus versicolor* | Ag | 25–75 | Spherical | Sanghi and Verma (2009) |
| *Fusarium oxysporum* | $PbCO_3$, $CdCO_3$ | 120–200 | Spherical | Sanyal et al. (2005) |
| *Fusarium oxysporum* | $SrCO_3$ | 10–50 | Needle like | Rautaray et al. (2004) |
| *Brevibacterium casei* | PHB | 100–125 | – | Pandian et al. (2009) |
| *Yeasts* | $Zn_3(PO_4)_2$ | 10–80 | Rectangular | Yan et al. (2009) |
| *Fusarium oxysporum* | CdSe | 9–15 | Spherical | Kumar et al. (2007) |
| *Aspergillus fumigatus* | ZnO | 1.2–6.8 | Spherical and hexagonal | Raliya and Tarafdar (2013) |
| *Aspergillus oryzae* | $FeCl_3$ | 10–24.6 | Spherical | Raliya (2013) |
| *Aspergillus tubingensis* | $Ca_3P_2O_8$ | 28.2 | Spherical | Tarafdar et al. (2012) |
| *Rhizopus oryzae* | Au | 10 | Nanocrystalline | Das et al. (2009) |
| *Aureobasidium pullulans* | Au | 29 ± 6 | Spherical | Zhang et al. (2011) |
| *Colletotrichum* sp. | Au | 20–40 | Decahedral and icosahedral | Shankar et al. (2003b) |
| *Helminthosporium solani* | Au | 2–70 | Polydispersed | Kumar et al. (2008) |
| *Neurospora crassa* | Au | 32 | Spherical | Castro-Longoria et al. (2011) |
| *Penicillium brevicompactum* | Au | 10–50 | Spherical | Mishra et al. (2011) |
| *Verticillium luteoalbum* | Au | <10 | Spheres and rods | Gericke and Pinches (2006) |
| *Cylindrocladium floridanum* | Au | 19.5 | Spherical | Narayanan and Sakthivel (2013) |
| *Coriolis versicolor* | Au | 20–100 | Spherical and ellipsoidal | Sanghi and Verma (2010) |
| *Verticillium* sp. | Ag | 25 | Spherical | Mukherjee et al. (2001) |
| *Aspergillus fumigatus* | Ag | 5–25 | Mostly spherical, triangular | Bhainsa and Souza (2006) |
| *Pleurotus sajorcaju* | Ag | 30.5 | Spherical | Vigneshwaran and Kathe (2007) |

(continued)

**Table 8.2** (continued)

| Bacteria | Nanoparticle | Size | Morphology | References |
|---|---|---|---|---|
| *Aspergillus flavus* | Ag | 8.92 | Spherical | Vigneshwaran et al. (2007) |
| *Trichoderma asperellum* | Ag | 13–18 | Nanocrystalline | Mukherjee et al. (2008) |
| *Penicillium fellutanum* | Ag | 5–25 | Mostly spherical | Kathiresan et al. (2009) |
| *Penicillium strain* J3 | Ag | 10–100 | Mostly spherical | Maliszewska et al. (2009) |
| *Cladosporium cladosporioides* | Ag | 10–100 | Mostly spherical | Balaji et al. (2009) |
| *Phoma glomerata* | Ag | 60–80 | Spherical | Birla et al. (2009) |
| *Coriolus versicolor* | Ag | 25–75 | Spherical | Sanghi and Verma (2009) |
| *Trichoderma viride* | Ag | 5–40 | Spherical, rodlike | Fayaz et al. (2009) |
| *Amylomyces rouxii* KSU-09 | Ag | 5–27 | Spherical | Musarrat et al. (2010) |
| *Aspergillus flavus* NJP08 | Ag | 17 | Spherical | Jain et al. (2011) |
| *Aspergillus terreus* CZR-1 | Ag | 2.5 | Spherical | Raliya and Tarafdar (2012) |
| *Fusarium oxysporum* | Au-Ag | 8–14 | Quasi-spherical | Senapati et al. (2005) |
| *Verticillium* sp. | $Fe_3O_4$ | 100–400 | Cubo-octahedral, quasi-spherical | Bharde et al. (2006) |
| *Aspergillus flavus* | $TiO_2$ | 62–74 | Spherical | Rajakumar et al. (2012) |
| *Aspergillus flavus* TFR7 | $TiO_2$ | 12–15 | Extracellular | Raliya et al. (2015) |
| *Fusarium* spp. | Zn | 100–200 | Irregular, spherical | Velmurugan et al. (2010) |
| *Aspergillus versicolor* | Hg | 20.5 | Alteration | Das et al. (2008) |
| **Algae** | | | | |
| *Shewanella algae* | Au | 9.6 | Spherical | Sau and Murphy (2004) |
| *Sargassum muticum* | Zn | 30–57 | Spherical | Azizi et al. (2014) |
| *Chlorococcum humicola* | Ag | 16 | | Jena et al. (2013) |
| *Plectonemaboryanum* | Pt | <300 | Spherical | Lengke et al. (2006) |
| *Sargassum bovinum* | Pd | 5–10 | | Momeni and Nabipour (2015) |
| *Phormidium tenue* | Cd | 5.1 | | MubarakAli et al. (2012) |
| *Phormidium valderianum* | Ag | 15 | | Parial et al. (2012) |
| *Chlorella vulgaris* | Ag | 44 | | Xie et al. (2007) |
| *Chlorella pyrenoidusa* | Au | 25–30 | | Oza et al. (2012) |

play significant roles by working as reducing agents. Moreover, these provide natural topping to synthesize MNPs, thus avoiding the accumulation with and increasing stability of MNPs. In recent research, bacteria, including *Pseudomonas deceptionensis* (Jo et al. 2015), *Weissella oryzae* (Singh et al. 2015), *Bacillus methylotrophicus* (Wang et al. 2015), *Brevibacterium frigoritolerans* (Singh et al. 2016), and *Bhargavaea indica* (Singh et al. 2015), have been explored for synthesis of Ag and Au NPs. Similar potential for producing NPs has been showed by using several *Bacillus* and other species, including *B. licheniformis, B. amyloliquefaciens, Rhodobacter sphaeroides*, *Listeria* monocytogenes, *B. subtilis*, and *Streptomyces anulatus*. Various genera of microorganisms have been reported for metal nanoparticle synthesis, including *Bacillus, Pseudomonas, Klebsiella, Escherichia, Enterobacter, Aeromonas, Corynebacterium, Lactobacillus, Pseudomonas, Weissella, Rhodobacter, Rhodococcus, Brevibacterium, Streptomyces, Trichoderma, Desulfovibrio, Sargassum, Shewanella, Plectonemaboryanum, Rhodopseudomonas, Pyrobaculum*, etc. These investigations suggest that the main mechanism of the synthesis of nanoparticles using bacteria depends on enzymes, for instance, the nitrate reductase enzyme was found to be responsible for silver nanoparticle synthesis in *B. licheniformis* (Singh et al. 2016).

Rather than using bacteria, mycosynthesis is a straightforward approach for achieving stable and easy biological nanoparticle synthesis. Most fungi containing important metabolites with higher bioaccumulation ability and simple downstream processing are easy to culture for the efficient, low-cost production of nanoparticles. Moreover, compared with bacteria, fungi have higher tolerances to, and uptake competences for, metals, particularly in terms of the high wall-binding capability of metal salts with fungal biomass for the high-yield production of nanoparticles. Three possible mechanisms have been proposed to explain the mycosynthesis of metal nanoparticles: nitrate reductase action; electron shuttle quinones; or both. Fungal enzymes, such as the reductase enzymes from *Penicillium* species and *Fusarium oxysporum*, nitrate reductase, and /-NADPH-dependent reductases, were found to have a significant role in nanoparticle synthesis, similar to the mechanism found in bacteria. The synthesis of nanoparticles using actinomycetes has not been well explored, even though actinomycete-mediated nanoparticles have good monodispersity and stability and significant biocidal activities against various pathogens. The synthesis of silver, copper, and zinc nanoparticles using *Streptomyces* sp. has demonstrated that the reductase enzyme from *Streptomyces* sp. has a vital role in the reduction of metal salts. Similar to other microorganisms, yeasts have also been widely investigated for the extracellular synthesis of the nanoparticles on a large scale, with straightforward downstream processing. Furthermore, virus-mediated synthesis of nanoparticles is also possible. Viruses can be used to synthesize nanowires with functional components that are assembled for various applications, such as battery electrodes, photovoltaic devices, and super capacitors. Nanoparticles are slow with low productivity, and the recovery of nanoparticles requires downstream processing. Furthermore, problems related to microorganism-based synthesis for nanoparticles also include the complex steps, such as microbial sampling, isolation, culturing, and maintenance.

## 8.5 Conclusion

The green method for nanoparticle synthesis, which is rapidly replacing traditional chemical syntheses, is of great interest because of eco-friendliness, economic views, feasibility, and a wide range of applications in several areas such as nano-medicine and catalysis medicine. Recently, various types of biological units which serve a dual role as both the reducing and stabilizing agents have been used in the synthesis of bioactive nanoparticles.

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