# Biogenic Synthesis of Metal Nanoparticles by Plants

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**Abstract**

Progressing in time proved development in technology that showed the ability of metals of nanoscale to perform specific utilities better than the bulk form of metals. Nanotechnology by means of specific traits of nanoparticles can be an identical valuable knowledge in various industry and science divisions. The noble metals like silver, gold, platinum, palladium, copper, zinc, selenium, titanium, and iron were used in synthesis of particles of nano-size. Chemical, physical, and biological ways have been used toward synthesis of various types of metal nanoparticles. The extensive potential applications of these nanoparticles made the green (biological or biogenic) synthesis by using bacteria, algae, actinomycetes, fungi, and plants. In the plant-based synthesis, several extracts (leaves, bark, stem, shoots, seeds, latex, secondary metabolites, roots, twigs, peel, fruit, seedlings, essential oils, tissue cultures, gum) are used. Therefore, the current review especially focuses on synthesis particularly plant-intermediated biosynthesis of metal nanoparticles and their classification.

**Keywords**

Green nanotechnology · Green nanoparticles · Biogenic nanoparticles · Nanoparticles production

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## 27.1 Introduction

### 27.1.1 Definition of Nanotechnology and Its Background

The term "nano" in the Greek language means small and dwarf. Each nanometer is numerically $10^{-9}$ or 1 billionth or as large as the three atomic widths that lie next to each other. In comparison, the size of DNA is over 2, proteins 50, influenza virus 100, and human hair diameter 10,000 nm. Nanotechnology is the foundation of many new technologies and innovations in the twenty-first century. New science of nanotechnology with Richard Feynman's famous speech, entitled "There are plenty of spaces around it" at the annual conference of the Physics Society of America in 1959, was established. Over the past few years, nanotechnology has come into various research areas and even human lives. Research and development is growing rapidly around the world. Nanotechnology refers to the ordering of atoms and molecules to the extent that new buildings form and lead to the production of materials and tools with new or even completely different properties.

Nanotechnology promotes the living standards of human beings and has great effects on the improvement and development of human security, welfare, and human health. Increasing the productivity using limited resources and energy sources will be the result of the application of this knowledge. Nanotechnology will discourse issues at the scale of disease causation and has a great potential for identifying and eliminating pathogens. Nanotechnology allows the use of drug release systems that can remain active over a period of time. Nanotechnology as a powerful technology enables humans to have a molecular and atomic attitude and can build nanoscale structures. Given the potential of nanotechnology, most countries use this technology as a tool for advancement in the world and taking the ground for "development leap" and counting it in line with their economic and national interests (Solgi et al. 2009, 2011; Dubey et al. 2010; Kaushik et al. 2010; Solgi 2012, 2014; Mukhopadhay 2014).

The income produced through worldwide nanotechnology increased quickly, presently around $39.2 billion, and is estimated to reach $90.5 billion in 2021 (McWilliams 2016; Rai et al. 2018). Nanotechnology has developed one of the most favorable technologies functional in all areas of knowledge. Metal nanoparticles created by nanotechnology have established universal attention as a result of their widespread applications in the physiochemical and biomedical grounds. Lately, producing metal nanoparticles by plants and microorganisms has been widely studied and has been documented as a green (biological) and competent way for additional using of microorganisms as suitable nano-factories (Singh et al. 2016).

### 27.1.2 Type of Nanostructures

Nanotechnology includes various subunits like nanotubes such as carbon nanotubes (CNTs), nanosensors, and nanomaterials. Each of them has many applications in industry, medicine, biosciences, agriculture, and natural resources. Nanomaterials

(NMs) also include subunits, one of the most important and most practical ones being metal nanoparticles. In fact, nanoparticles of metals are the most important product of nanotechnology. Nanoparticles are called the particles which have all the same dimensions, and their sizes are less than 100 nm. Metal nanoparticles have been very much considered for optical, catalytic, magnetic, and electrical properties (Dubey et al. 2010; Kaushik et al. 2010; Solgi et al. 2011; Solgi 2012).

Nanometals like gold, silver, platinum, copper, zinc, palladium, and iron were used in synthesis of particles of nano-size. The nanoparticle properties such as shape, size, structure, and crystalline nature determine their applications. The nanoparticles (NPs) are metal atom clusters with a range of 1–100 nm, extremely favorable due to their extensive range of requests in profitable products. The metal nanoparticles are synthesized by physical, chemical, and biological approaches. The biological synthesis of nanoparticles involves plants, bacteria, fungi, algae, and actinomycetes (Haleemkhan et al. 2015).

### 27.1.3 Nanoparticle Synthesis

#### 27.1.3.1 Physical Procedures

Laser ablation, condensation evaporation, diffusion, electrolysis, pyrolysis, and high-energy ball milling are the components of metal nanoparticle manufacturing (Iravani et al. 2014). In laser ablation, colloidal nanoparticles are commonly produced using several solvents. The pulsed laser ablation in liquid (PLAL) is done within the chamber under vacuum along with a number of inert gases (Khodashenas and Ghorbani 2014). The lack of chemical reagents in solutions is the main benefit of PLAL than other methods for production of metal colloids (Iravani et al. 2014). Many nanoparticles, including Au and Ag, have been produced by evaporation-condensation method. However, it is associated with several disadvantages; for example, it occupies a huge space and takes time to gain thermal stability and also consumes a large amount of energy while raising the environmental temperature around the source material (Hong and Han 2006; Korbekandi et al. 2015).

Spray pyrolysis for the production of nanoparticles has been developed recently, and its flexibility in synthesis of particles with different appearances, sizes, and compositions has been approved (Hongwang and Swihart 2007). High-impact collisions are applied in high-energy ball milling for reducing macroscale or microscale materials into nano-crystalline structures with no chemical changes (Vijayaraghavan and Ashokkumar 2017).

#### 27.1.3.2 Chemical Methods

Chemical reduction, micro-emulsion/colloidal, and electrochemical and thermal decomposition are the available chemical systems to manufacture nanoparticles. Chemical reduction using organic and inorganic reducing agents has been shown as the commonly used method for producing colloidal metal particles, since it is equipped with simple tools and also its simple function. Potassium bitartrate, sodium borohydride, methoxy polyethylene glycol, trisodium citrate dihydrate, ascorbate, and elemental hydrogen are the most commonly used reducing mediators (Tan et al. 2003; Kim et al. 2007; Mallick et al. 2004; Rivas et al. 2001; Iravani et al. 2014; Merga et al. 2007). Such chemical materials can reduce metallic ions like gold, silver, and lead for producing corresponding metallic nanoparticles.

Micro-emulsion technique is an adaptable and repeatable technique to manage particle's feature, including shape, size, surface area, and homogeneity (Malik et al. 2012). Size and morphology of the nanoparticles have been widely tried to be controlled via micro-emulsion method (Martínez-Rodríguez et al. 2014). Electricity is employed as a controlling force to produce nanoparticles via electrochemical methods. Accordingly, passing an electric current among two electrodes divided by an electrolyte and also nanoparticle production occurred at the electrode/electrolyte interface (Starowicz et al. 2006). Electrochemical method was employed by Rodríguez-Sánchez et al. (2000) according to the dissolution of a metallic anode in an aprotic solvent for preparing Ag nanoparticles (2–7 nm). In addition, they stated that different Ag particle sizes can be obtained via changing the current density. Thermal decomposition technique is widely used for synthesis of stable monodisperse suspensions with self-assembly (Simeonidis et al. 2007).

In general, size and the composition of the obtained nanoparticles are associated with temperature, reaction time, and surfactant molecule length. Although chemical synthesis technique has many advantages, using extreme surfactants, solvents, and other chemicals prevents the application aspects of produced nanoparticles (Vijayaraghavan and Ashokkumar 2017).

#### 27.1.3.3 Biological Methods

Biological resources have been considered to produce metallic nanoparticles for developing cost-effective and eco-friendly method. Green (biological) synthesis includes the reduction of metal ions by biological mass/extract as the resultants. Moreover, eco-friendliness and cost-effectiveness as the advantages of biological method than the traditional chemical and physical methods indicate its efficacy for catalyzing reactions in aqueous media at a standard temperature and pressure and also the flexibility of the process (Schrofel et al. 2014). The reduction occurred by components available in biological materials, and it is mostly activated by several compounds seen in the cell, like carbonyl, phenolic, amine, proteins, amide groups, pigments, flavonoids, terpenoids, alkaloids, and other reducing materials (Asmathunisha and Kathiresan 2013). Due to the varied structure in these groups, the exact mechanism for biosynthesis of nanoparticles is not easy to explain and has not yet been entirely identified. Bacteria, fungi, yeast, virus, algae, and plant extract/biomass are crucial biological compounds applied to form metallic nanoparticles (Lombardi and Garcia Jr 1999).

Bacteria are the main group of unicellular living organisms (from prokaryotes), found in water and soil (Vijayaraghavan and Yun 2008; Vijayaraghavan and Balasubramanian 2015). Different bacterial genera (*Bacillus* and *Pseudomonas*) have been studied for biosynthesis of nanomaterials (Kalishwaralal et al. 2009; Phadke and Patel 2012). Nanometals Au and Ag were obtained by Nair and Pradeep (2002) through the reaction of the corresponding metal ions within cells of lactic acid bacteria found in buttermilk. In addition, Husseiny et al. (2007) evaluated extracellular production of Au nanoparticles by *Pseudomonas aeruginosa*. Kalimuthu et al. (2008) also produced Ag nanoparticles through *Bacillus licheniformis*. Inactive and/or dead bacterial biomasses have been found to reduce metal ions to nanoparticles due to the certain organic functional groups on the cell wall.

Fungi are eukaryotic and non-phototrophic microorganisms characterized by a firm cell wall. Their cell wall contains polysaccharides and glycoproteins, in which chitin and glucan are commonly found (Yadav et al. 2015). Production of metal nanoparticles is done extracellularly or intracellularly by fungi (Mukherjee et al. 2001). Extracellular synthesis is much rapid compared to the intracellular route (Narayanan and Sakthivel 2010a). Several studies have demonstrated fungi synthesizing nanoparticles extracellularly, namely, *Fusarium solani* (Ingle et al. 2009), *Penicillium fellutanum* (Kathiresan et al. 2009), *Phoma glomerata* (Birla et al. 2009), *Aspergillus oryzae* (Binupriya et al. 2010), *Aspergillus terreus* (Baskar et al. 2013), and *Rhizopus nigricans* (Ravindra and Rajasab 2013). On the contrary, limited investigations have been done on the intracellular synthesis of nanoparticles by fungal species (Mukherjee et al. 2001).

Algae are simple organisms, in which several specific structures and organs in earthly plants cannot be found. Using algae for production of metal nanoparticle has not widely been considered. Application of microalgae in producing nanoparticles has been negligibly reported (Sudha et al. 2013; Jena et al. 2014). The brown marine algae (*Sargassum wightii*) have shown useful for synthesizing gold nanoparticles extracellularly. Additional brown seaweeds, including *Turbinaria conoides*, green seaweeds, as well as red seaweeds have also been investigated for nanoparticle production (Rajeshkumar et al. 2013; Sangeetha et al. 2013; Priyadharshini et al. 2014).

#### 27.1.3.3.1 Advantage of Biological Nanoparticles

Reducing metal cytotoxicity is crucial for metal nanoparticles for biomedical uses. Metal nanoparticles obtained by green (biogenic) routes are free from toxicity of by-products than the physicochemical-derived nanoparticles (Solgi and Taghizadeh 2012; Baker et al. 2013).

The green or biological production of nanoparticles is associated with several advantages, such as eco-friendly and rapid production methods and the cost-effective and biocompatible type of produced nanoparticles. In addition, there is no need for more stabilizing agents, since microorganism and plant components act as stabilizing agents (Makarov et al. 2014). Biological nanoparticles are more active due to the binding of biologically active components on the surface of synthesized nanoparticles from the biological sources, like microorganisms and plants. Many abundant metabolites with pharmacological effects are available and found to bind to the synthesized nanoparticles, providing supplementary profit through the increased effectiveness of the nanoparticles, especially in medicinal plants (Makarov et al. 2014; Singh et al. 2016). Moreover, by biological synthesis the needed steps can be reduced, for example, the attachment of some functional groups to the nanoparticle surface for making them biologically active, which is an additional step for physiochemical production (Baker et al. 2013). Time of biosynthesizing nanoparticles is also lower than that of the physiochemical methods. High-speed synthetic methods have developed with high yields via development of different plant sources. For example, silver nanoparticles (SNPs) have been synthesized via different plant extracts through 2, 5, and 45 min. Gold nanoparticles have also been shown to be produced within 3 and 5 min, indicating the simple and fast synthesis of nanoparticles by plant extracts (Lombardi and Garcia Jr 1999; Vijayaraghavan and Yun 2008; Priyadharshini et al. 2014; Singh et al. 2016).

#### 27.1.3.3.2 Plant-Mediated Synthesis (Phytosynthesis) of Nanoparticles

Using plants or their extracts for synthesis of nanoparticles has been considered in nanotechnology as an environmentally friendly method. The basic green (biological) chemistry principles make cleaner synthesis of nanoparticles. Biological synthesis (phytosynthesis) applies molecular tolerance mechanisms and metabolomics to form nanoparticles (Rai et al. 2018).

Phytonanotechnology has recently offered new methods to synthesize nanoparticles, which are cost-effective, simple, high speed, eco-friendly, and stable. Biological synthesis using plants is associated with several benefits, including scalability, biocompatibility, and the medical use of synthesizing nanoparticles using the water, common solvent, as a reducing medium (Noruzi 2015). Therefore, plant-mediated nanoparticles derived from readily accessible plant materials and the plants' safety are both effective to achieve the high demand for nanoparticles to use in the environmental and biomedical settings. Accordingly, it has been tried to investigate various plant species to assess their potential to synthesize nanoparticles. Different plant parts, such as roots, stems, leaves, fruits, flowers, and their extracts, have been applied to produce metal nanoparticles. Table 27.1 shows some of these sections/extracts. The underlying mechanism and the components essential for plant-mediated synthetic nanoparticles have not yet been demonstrated. Proteins, amino acids, organic acid, and vitamins and also secondary metabolites, including flavonoids, alkaloids, polyphenols, terpenoids, heterocyclic compounds, and polysaccharides, have been shown effective in metal salt reduction. They also act as capping and stabilizing factors to form nanoparticles (Duan et al. 2015). In this regard, Solgi (2014) found that saffron petal extract includes phenolic compounds, including flavonoids (kaempferol) and anthocyanins (anthocyanidin, delphinidin, and pelargonidin). In addition, Solgi indicated that pomegranate peels have phenolic compounds, including ellagic acid and quercetin, quercitrin, rutin, luteolin, gallic acid, and myricetin, found in fresh flowers of Damask rose (Solgi and Taghizadeh 2012). Their hydroxyl groups are able to attach silver ions and affect the biosynthesis of SNPs and also act as reducing agent for the reduction of silver ions (Ag+) to SNPs (Ag0) (Solgi and Taghizadeh 2012; Solgi 2014). Furthermore, El-Kassas and El-Sheekh (2014) reported that the hydroxyl functional group of the polyphenols as well as the carbonyl group of proteins of *Corallina officinalis* extract are associated with producing and stabilizing gold nanoparticles. Philip et al. (2011) demonstrated formation and stabilization of silver and gold nanoparticles via biomolecule attachment in leaf extract of *Murraya koenigii*. It has stated that various mechanisms to synthesize nanoparticles are found in several plant species (Baker et al. 2013).

**Table 27.1** Biological synthesis of several metal/metal-oxide nanoparticles by different plant parts

| Plant name | Plant section | Nanoparticle name | Size (nm) | References | Year |
|---|---|---|---|---|---|
| *Geranium graveolens* | Leaves | Silver | 27 | Shankar et al. | 2003 |
| *Aloe vera* | Leaves | Silver and gold | 15–20 | Chandran et al. | 2006 |
| *Carica papaya* | Fruits | Silver | 15 | Jain et al. | 2009 |
| *Rosa rugosa* | Leaves | Silver and gold | Silver, 11; gold, 12 | Dubey et al. | 2010 |
| *Coleus amboinicus* | Leaves | Gold | 4.6–55 | Narayanan and Sakthivel | 2010a, b |
| *Capsicum annuum* | Fruits | Silver | 2–6 | Jha and Prasad | 2011 |
| *Rosa damascena* | Petals | Silver | 13–28 | Solgi | 2012 |
| *Punica granatum* | Peel | Silver | 19–29 | Solgi | 2012 |
| *Anogeissus latifolia* | Gum powder | Silver | 5.5–5.9 | Kora et al. | 2012 |
| Banana | Peel | Cadmium sulfide | 1.48 | Zhou et al. | 2014 |
| *Crocus sativus* | Petals | Silver | 2–3.5 | Solgi | 2014 |
| *Euphorbia prostrata* | Leaves | Silver and titanium dioxide ($TiO_2$) | Silver, 10–15; $TiO_2$, 81.7–84.7 | Zahir et al. | 2015 |
| *Ginkgo biloba* | Leaves | Copper | 15–20 | Nasrollahzadeh and Sajadi | 2015 |
| *Panax ginseng* | Root | Silver and gold | Silver, 10–30; gold, 10–40 | Singh et al. | 2015 |
| *Azadirachta indica* | Leaves | Silver | 41–60 | Poopathi et al. | 2015 |
| *Cocos nucifera* | Leaves | Lead | 47 | Elango and Roopan | 2015 |
| *Pistacia atlantica* | Seeds | Silver | 27 | Sadeghi et al. | 2015 |
| *Citrus medica* | Fruits | Copper | 20 | Shende et al. | 2015 |
| *Lawsonia inermis* | Leaves | Iron | 21 | Naseem and Farrukh | 2015 |
| *Origanum vulgare* | Leaves | Titanium dioxide ($TiO_2$) | 2–15 | Shiak et al. | 2018 |
| *Thymus vulgaris* | Waste extract (leaves and stems) | Zinc oxide (ZnO) | 10–35 | Abolghasemi et al. | 2019 |

Eugenol as the certain terpenoid in *Cinnamomum zeylanisum* plays a crucial role in the synthesis of gold and SNPs (Makarov et al. 2014). It should be noted that dicot plants have different secondary metabolites possibly effective for nanoparticle synthesis (Singh et al. 2016).

## 27.2 Characterization of Nanoparticle

Several experimental methods have been employed to observe, form, and characterize metallic nanoparticles.

### 27.2.1 UV-VIS Spectroscopy

UV-visible spectroscopy (UV-Vis) method is applied to quantify the light absorbed or scattered by a sample. It has widely accepted that UV-Vis spectra can be applied for evaluating the size and shape of the controlled nanoparticles in aqueous suspensions. UV-Vis is employed for determining the concentration of the elements in solutions, namely, silver, gold, and copper. In this respect, it is used for detecting and evaluating the possibility of producing nanoparticles of metals, including silver, and its concentration in a watery environment. A wavelength of 200–700 nm is commonly applied for determination of the nanoparticle production from metals. For example, the exact wavelength peak for absorption of silver and gold is 450 and 550 nm, respectively. Indeed, UV-Vis is a tool for measuring the absorption spectra of the samples (Jain et al. 2009; Jha et al. 2009; Dubey et al. 2010; Bankar et al. 2010; Krishnaraj et al. 2010; Solgi and Taghizadeh 2012; Solgi 2014).

### 27.2.2 *FTIR* Spectroscopy

Fourier-transform infrared (FTIR) spectroscopy is developed for measuring the chemical bonds in surface atoms of plant samples and functional atoms involved in the recovery of nanomaterials and their production as well. FTIR with infrared light irradiation makes the molecular bands vibrate leading to design the graph. The obtained graph includes different absorption peaks, each of them shows specific chemical bonds. The infrared spectroscopy (IR spectroscopy) device to detect chemical groups is involved in the formation of SNPs. For instance, the chemical carbonyl group has a peak of approximately 11,700 cm (Jain et al. 2009; Jha et al. 2009; Dubey et al. 2010; Bankar et al. 2010; Krishnaraj et al. 2010; Solgi and Taghizadeh 2012; Solgi 2014).

### 27.2.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) method is the commonly used procedure for measuring the morphology, size, and size distribution of the metal nanoparticles.

### 27.2.4 Scanning Electron Microscopy(SEM)

A scanning electron microscope is applied for determining the shape or precision for evaluating the size of nanomaterials formed in the nanometer size and also for assessing their shapes. For TEM, nearly 25 μl of the samples is removed coating on copper rod, followed by transmitting SNPs using an electron microscope (Jain et al. 2009; Jha et al. 2009; Dubey et al. 2010; Bankar et al. 2010; Krishnaraj et al. 2010; Solgi and Taghizadeh 2012; Solgi 2014).

### 27.2.5 X-Ray Diffraction (XRD)

XRD system is a useful tool for analyzing the crystal structure as well as mean particle size of the nanoparticles. It is used for the quantitative and qualitative measurement of the solid and liquid phases. Accordingly, dried SNPs are covered on the roll of the apparatus, and the spectrum is then set at 40 kV voltages and 30 mAh current and the element's radiation is transmitted. Scherrer equation was developed for calculation of the crystallite size from XRD diffraction pattern for nanoparticles:

$$d = \mathrm{K}\lambda / B\cos\ \theta$$

where

D = mean dimension of crystallites (nm)
$\lambda$ = X-ray radiation wavelength
K = Scherrer constant (morphology, commonly 0.94)
$B$ = the line full width at half maximum (FWHM) height in radians
$\theta$ = Bragg angle (the position of the diffraction peak maximum)

(Jain et al. 2009; Jha et al. 2009; Dubey et al. 2010; Bankar et al. 2010; Krishnaraj et al. 2010; Solgi and Taghizadeh 2012; Solgi 2014).

### 27.2.6 Energy Dispersive X-Ray Spectroscopy (EDS or EDX)

EDX spectroscopy is an appropriate method for identification, purity, and the elemental composition of the formed nanoparticles. The shape and chemical composition of the resulted nanoparticles are assessed through scanning electron microscopy (SEM), which is equipped with an energy-dispersive X-ray spectrometer (EDX or EDS) (Jain et al. 2009; Jha et al. 2009; Dubey et al. 2010; Bankar et al. 2010; Krishnaraj et al. 2010; Solgi and Taghizadeh 2012; Solgi 2014).

## 27.3 Nanoparticles and Their Applications

Nanotechnology has known as one of the most crucial technologies in all academic fields. Nanomaterials have been applied unknowingly for a long period of time. For instance, gold nanoparticles used for staining drinking glasses also have treated several disorders. In recent years, the different uses of metal nanoparticles have been considered in many fields, including biomedical, agricultural, environmental, and physiochemical fields (Solgi et al. 2009, 2011; Solgi 2014). Gold nanoparticles have shown to be used for the specific delivery of mediations, like methotrexate. They have also been found effective to diagnose genetic disorders, detect tumors, and also use for photoimaging. It has been shown that iron oxide nanoparticles are useful for drug delivery, treatment of cancer, tissue repair, cell labeling, targeting and immunoassays, detoxification of biological fluids, magnetic resonance imaging, and magnetically responsive drug delivery therapy (Singh et al. 2016). SNPs recently have been extensively considered due to their increasing application in various areas, including textiles, electronics, pharmaceutics, cosmetics, and environmental remediation. They have also been employed for many antimicrobial applications. Anticancer, anti-inflammatory, and wound healing are other uses of SNPs (Solgi et al. 2009, 2011; Ahamed et al. 2010). Considering their nontoxic, biocompatible, self-cleansing, skin-compatible, antimicrobial, and dermatological effects, zinc and titanium nanoparticles have been applied in cosmetic, biomedical, and ultraviolet (UV)-blocking agents (Zahir et al. 2015; Singh et al. 2016). In addition, metal nanoparticle has been used in the spatial analysis of different biomolecules, such as peptides, nucleic acids, lipids, fatty acids, glycosphingolipids, and molecules of drug to image these molecules with higher sensitivity and spatial resolution (Nasrollahzadeh et al 2014).

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