

Green Synthesis of silver nanoparticles involving extract of plants of different taxonomic groups

Abstract

Silver nanoparticles are being used in numerous technologies and incorporated into a wide array of consumer products that take advantage of their desirable optical, conductive, and antibacterial properties. Silver nanoparticles have attained a special focus due to its antimicrobial property. Conventionally silver nanoparticles are synthesized by chemical method using chemicals as reducing agents which later on become accountable for various biological risks due to their general toxicity; engendering the serious concern to develop environment friendly processes. Thus, to solve the objective; principles of green chemistry have now become a torch for chemical technologist, biotechnologist and nanotechnologist worldwide in developing less hazardous chemicals. The present review explores the synthesis of silver nanoparticles through a natural and single step protocol preparatory method using the different plant products of different taxa belonging to different families with green principles over the conventional ones.

Keywords: Green synthesis, Silver nanoparticles, Plants extract, Precursor

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Introduction

Nanotechnology today is regarded as a revolutionary technology which deals with the matter at nanoscale (1-100 nm). Within this size range all the properties (chemical, physical and biological) changes in fundamental ways of both individual atoms/molecules and their corresponding bulk. Novel applications of nanoparticles and nanomaterials are growing rapidly on various fronts due to their completely new or enhanced properties based on size, their distribution and morphology. Nanotechnology is emerging as the sixth revolutionary technology in the current era. It is now emerging and fast growing field of science which is being exploited over a wide range of disciplines such as physics, chemistry, biology, material science, electronics, medicine, energy, environment and health sectors. The nanoparticles used for all the aforesaid purposes, the metallic nanoparticles considered as the most promising as they contain remarkable antibacterial properties due to their large surface area to volume ratio. Amongst the all noble metal nanoparticles, silver nanoparticles are significant which has gained boundless interests because of their unique properties such as chemical stability, good conductivity, catalytic and most important antimicrobial and anti-inflammatory activities.^{1,2} Silver's mode of action is presumed to be dependent on Ag⁺ ions, which strongly inhibit bacterial growth through suppression of respiratory enzyme and electron transport components and through interference with DNA functions³

Because of their wide range of applications Synthesis of silver nanoparticles is of much interest to the researcher. Generally, nanoparticles are prepared by a variety of chemical and physical methods which are quite expensive and potentially hazardous to the environment which involve use of toxic chemicals that are responsible for various biological risks. In the search of cheaper and eco-compatible pathways for nanoparticles, scientist used microorganism⁴⁻¹¹ and plant extracts.¹²⁻¹⁵ Green synthesis of nanoparticles has proven to be better methods due to slower kinetics, offer better manipulation, control over crystal growth and their stabilization. Greener synthesis provides advancement over traditionally used nanoparticles synthesis methods i.e. chemical.^{16,17} and physical method as it is cost effective,

easily scaled up, environment friendly¹⁸ or large scale synthesis and in this method there is no need to use toxic chemicals. Green synthesis of nanoparticles is a bottom up approach where the main reaction occurring is reduction. Biogenic synthesis is useful not only because of its reduced environmental impact.¹⁹⁻²¹ compared with some of the physicochemical production methods, but also because it can be used to produce large quantities of nanoparticles that are free of contamination and have a well-defined size and morphology.²² Biosynthetic routes can actually provide nanoparticles of a better defined size and morphology than some of the physicochemical methods of production.²³ The methods for obtaining nanoparticles using naturally occurring reagents such as vitamins, sugars, plant extracts, biodegradable polymers, and microorganism as reductants and capping agents could be considered attractive for nanotechnology. But among above mentioned reagents plant extract using leaf, root, stem, latex, resin, seed seems to be the best candidates and they are suitable for large scale "Green synthesis" of nanoparticles. The advancement of green syntheses over chemical and physical methods is: environment friendly, cost effective and easily scaled up for large scale syntheses of nanoparticles, furthermore there is no need to use high temperature, pressure, energy and toxic chemicals.²⁴ Although, among the various biological methods of silver nanoparticle synthesis, microbe mediated synthesis is not of industrial feasibility due to the requirements of highly aseptic conditions and their maintenance. Therefore; the use of plant extracts for this purpose is potentially advantageous over microorganisms due to the ease of improvement, the less biohazard and elaborate process of maintaining cell cultures.²⁵

Hence, a review is compiled describing the green syntheses of silver nanoparticles that provide advancement over conventional methods as it is cost effective and lesser or almost zero contaminations for the environment.

Green synthesis of silver nps by plants

A large number of plants are reported to facilitate silver nanoparticles syntheses are mentioned in Table 1 and are discussed briefly in the presented review.

Table 1 Use of different plant parts extract in the synthesis of silver nanoparticles as a precursor

S. No.	Latin Name	Family Name	Size and Shape	References
Leaves Extract				
1	<i>Azadirachta indica</i>	Meliaceae	spherical	21
2	<i>Aloe vera</i>	Xanthorrhoeaceae	12.2nm, spherical	42
3	<i>Argemone maxicana</i>	Papaveraceae	16-40nm, crystalline	68
4	Tea	Theaceae	20 to 90 nm.	69
5	<i>Citrullus colocynthis</i>	Cucurbitaceae	31nm	49
6	<i>Cassia auriculata</i>	Caesalpiniaceae	20-40nm	70
7	<i>Coleus aromaticus</i>	Labiatae	44nm	51
8	<i>Myrica nagi</i>	Myricaceae	50-69nm	71
9	<i>Diopyros kaki</i>	Ebenaceae	15-500nm, cubic	45
10	<i>Euphorbia hirta</i>	Euphorbiaceae	40-50nm, spherical	72
11	<i>Ginko biloba</i>	Ginkgoaceae	15-500nm, cubic	45
12	<i>Helianthus annus</i>	Asteraceae		44
13	<i>Hibiscus rosasinensis</i>	Malvaceae	13nm, spherical	73
14	<i>Magnolia kobus</i>	Magnoliaceae	15-500nm, cubic	45
15	<i>Mangifera indica</i>	Anacardiaceae	20nm, spherical, triangular, hexagonal	74
16	<i>Mentha piperita</i>	Lamiaceae	90nm, spherical	76
17	<i>Memecylon edule</i>	Melastomataceae	50-90nm, square	77
18	<i>Murraya keenigii</i>	Rutaceae	10nm, crystalline, spherical	75
19	<i>Nicotiana tobaccum</i>	Solanaceae	8nm, crystalline	78
20	<i>Ocimum tenuiflorum</i>	Lamiaceae	5-10nm, spherical	26
21	<i>Oryza sativa</i>	Poaceae		44
22	<i>Pelargonium graveolens</i>	Geraniaceae	16-40nm, crystalline	41
23	<i>Piper betle</i>	Piperaceae	3-37nm, spherical	79
24	<i>Platanus orientalis</i>	Platanaceae	15-500nm, cubic	47
25	<i>Pinus desiflora</i>	Pinaceae	15-500nm, cubic	47
26	<i>Rosa rugosa</i>	Rosaceae	30-60nm	80
27	<i>Saccharum officinarum</i>	Poaceae		44
28	<i>Sorghum bicolor</i>	Poaceae		44
Seed Extract				
1	<i>Jatropha curcas</i>	Euphorbiaceae	10-20nm, crystalline	63
2	<i>Medicago sativa</i>	Fabaceae	5-51nm, spherical	65
3	<i>Papaver somniferum</i>	Papaveraceae		64
4	<i>Nyctanthes arbor-tristis</i>	Nyctanthes	50 and 80 nm, spherical	15
Fruit Extract				
1	<i>Emblica officinalis</i>	Euphorbiaceae	10-20 nm	38
2	<i>Carica papaya</i>	Caricaceae	15nm, cubic	12
3	<i>Tanacetum vulgare</i>	Asteraceae	16nm, spherical	80
Fruit Peel Extract				
1	<i>Musa pudica</i>	Musaceae	20nm	35
2	<i>Annona squamosa</i>	Annonaceae	20-60nm, spherical	36
3	<i>Citrus sinensis</i>	Rutaceae	14-20nm, spherical	81
4	<i>Punica granatum</i>	Punicaceae	5+1.5 nm	37
Gum and Latex				
1	<i>Jatropha curcas</i>	Euphorbiaceae		79
2	<i>Euphorbia</i>	Euphorbiaceae	18nm	26
3	<i>Acacia</i>	Mimosoideae		28
4	<i>Boswellia serrata</i>	Burseraceae		27
5	Peach gum	Rosaceae	23.56±7.87 nm	80
Bark/ Stem Powder				
1	<i>Cinnamon zeylanicum</i>	Lauraceae	31-40nm, spherical	60
2	<i>Shorea tumbuggaia</i>	Dipterocarpaceae	Spherical	61
3	<i>Boswellia ovalifoliolata</i>	Burseraceae	Spherical	61
Tuber, Root, Rhizome				
1	<i>Curcuma longa</i>	Zingiberaceae	21-30nm, quasi-spherical, triangular	58
2	<i>Dioscorea bulbifera</i>	Dioscoreaceae	8-20 nm, spherical, triangular	56
3	<i>Ocimum sanctum</i>	Lamiaceae	5-10nm, spherical	82
4	<i>Zingiber officinale</i>	Zingiberaceae	6-20nm, spherical	82
Coir Extract				
1	<i>Cocos nucifera</i>	Arecaceae	23+2nm	55
Flower Extract				
1	<i>Pandanus odorifer</i> Forssk (spath of male inflorescence)	Pandanaceae	24-55 nm, quasispherical	66
2	<i>Hibiscus sabdariffa</i> (flower)	Malvaceae		67

Preparation of plant broth and biosynthesis of silver nanoparticles

The protocol for the nanoparticle syntheses involves: the collection of the part of plant of interest from the available sites then it's washing thoroughly with tap water to remove contamination followed by surface sterilization with double distilled water and air dried at room temperature. These clean and fresh sources are then powdered using domestic blender or cut it into very small pieces. And for the plant broth preparation, around 10-25g of the dried powder or finally chopped leaves were kept in a beaker and boiled with 100mL of deionised distilled water. The extract was filtered with Whatman filter paper No.1 further the filtrate was used as reducing source for the synthesis of silver nanoparticles.

Synthesis of silver nanoparticles was carried out by adding 10ml of leaf extract to 100ml of 1mM silver nitrate (AgNO_3) solution with continuous stirring at room temperature. Reduction of Ag^+ to Ag^0 was confirmed by the colour change of solution from colourless to brown. Its formation was further confirmed by using UV-Visible spectroscopy.

Plant latex and gum as medium

Synthesized the silver nanoparticles in one-step solvent free condition using *Euphorbiaceae* plant latex.²⁶ Around eight plant species were utilized for the synthesis of nanoparticles, out of which *Jatropha gossypifolia*, *Jatropha curcas*, and *Euphorbia milii* showed an average of $62 + 105$ nm. The stem latex of *Boswellia serrata* was successfully used to induce synthesis of silver nanoparticles.²⁷ It has been demonstrated that the plant based exudates gum such as *gum Acacia* can be utilized as a reducing and stabilizing agent for the silver nanoparticle biosynthesis.²⁸ *Gum kondagogu* biopolymer derived as exudates from the bark of *Cochlospermum gossypium* used as a template for the synthesis and stabilization of silver nanoparticles. The synthesis was carried out in aqueous medium without the requirement of any added chemical reducing agent by autoclaving. *Gum olibanum* is a naturally occurring gum-oleo-resin derived as exudates from the bark of *Boswellia serrata*, a native tree of India. Besides its use as incense, fumigant and multipurpose aromatic; it is also exploited in silver nanoparticle synthesis as reducing and capping agent. Typically the gum consists of volatile oil, water soluble gum (polysaccharides), lipophilic terpenes and insoluble matter. The polysaccharide is abundant in neutral sugars and composed of galactose, arabinose, xylose and d-glucuronic acid.^{29,30} From the Raman spectrum of the nanoparticle solution it is confirmed that both amino and carboxylate groups of the gum are involved in the capping of the nanoparticles.²⁷

Fruit peel extracts as medium

Literature survey has shown that naturally available agricultural wastes have not been investigated for the synthesis of silver nanoparticles. A classical example of such an abundantly available natural material is the banana peel. Bananas are consumed all over the world. After consumption of the pulp, the peels are generally discarded. Beside a few applications of banana peels i.e. exploitation of their medicinal properties,³¹ in ethanol fermentation,³² as a substrate for generating fungal biomass,³³ utilization as a biosorbent for heavy metal removal.^{34,35} utilizes banana peel for the synthesis of silver nanoparticles.³⁶ employing peel extract of *Annona squamosa* for the synthesis of silver nanoparticles. Controlled growth of silver nanoparticles was formed in 4hr at room temperature (25°C) and 60°C. silver nanoparticles were irregular spherical in shape and the average particle size was about 35 ± 5 nm. The water soluble ketone and hydroxyl as functional group containing compounds are reported

to be responsible for the reduction of silver ions.³⁶ The Pomegranate fruit extract is a rich source of highly potent antioxidants due to rich in phenolic compounds (mainly Ellagic acid) employed for the synthesis of silver nanoparticles. Ellagic acid an active constituent present in fruit peel has an easy electron losing capacity which results in the formation of H^+ radical, which reduces the size of silver to nano size. The morphological and crystalline phase study of the NPs showed that the average size of silver nanoparticles obtained from was 5 ± 1.5 nm.³⁷

Fruit extract as medium

On treating aqueous silver sulfate and chloroauric acid solutions with *Embllica Officinalis* fruit extract, rapid reduction of the silver and chloroaurate ions is observed leading to the formation of highly stable silver and gold nanoparticles in solution. Transmission Electron Microscopy analysis of the silver and gold nanoparticles indicated that they ranged in size from 10 to 20 nm and 15 to 25 nm respectively.³⁸ The fruit extract of papaya works as reducing as well as capping agent. Nanoparticles on characterization analysis showed the average particle size of 15 nm as well as revealed their cubic structure. C-O group of polyols such as hydroxyl flavones and catechins present in green unripe Papaya (*Carica papaya*) fruit are mainly responsible for the reduction of Ag ions, whereby they themselves get oxidized to unsaturated carbonyl groups.¹²

Leaf extract as medium

The synthesis of quasi-spherical silver nanoparticles and triangular or spherical gold nanoparticles using sun dried *Cinnamomum camphora* leaf without addition of any protectors or accelerators.³⁹ They demonstrated that the polyol components and water soluble hydrocyclic compounds present in leaf were mainly responsible for reduction of silver ions or chloroaurate ions.⁴⁰ Reported the possibility of terpenoids from geranium leaf in the synthesis of nano-sized silver particles.⁴¹ Reported the synthesis of highly stable and crystalline silver nanoparticles (16-40 nm) by exposing the aqueous geranium leaf extract to silver nitrate solution. Highly concentrated silver nanoparticles obtained from the aqueous leaf extract of *Azadirachta indica*.²¹ Leela A & Song JY.^{42,43} reported the synthesis of silver nanoparticles from the leaf extracts of *Aloe vera* and *Capsicum annum* plants, respectively. Among the leaf extracts of plants, namely, *Helianthus annuus*, *Basella alba*, *Oryza sativa*, *Saccharum officinarum*, *Sorghum bicolor*, and *Zea mays*, it is concluded that among all the tested plant extracts, *H. annuus* exhibited the strongest potential for rapid reduction of silver ions.⁴⁴ Leaf extract of Pine, Persimmon, Ginkgo, Magnolia, and Platanus plants is used for the extracellular synthesis of silver nanoparticles.⁴⁵ Methanolic extract of *Eucalyptus* hybrid leaves is exploited in the extracellular biosynthesis of silver nanoparticles.⁴⁶ Similarly, Satyavani K.⁴⁷ reported rapid synthesis (reaction time <30 min) of silver nanoparticles using *Acalypha indica* leaf extract and their antibacterial activity against water borne pathogens. Patil RS.⁴⁸ Highlighted the possibility of tissue culture-derived callus extract from *Sesuvium portulacastrum* for the synthesis of antimicrobial silver nanoparticles. Similarly,⁴⁹ reported the synthesis of silver nanoparticles using the stem-derived callus extract of the bitter apple plant and illustrated their tremendous antibacterial activity. Very recently, bio-inspired synthesis of highly stabilized silver nanoparticles using *Ocimum tenuiflorum* as well as *Coleus aromaticus* have been reported by.^{31,50,51} respectively. Kulkarni AP.⁵² Synthesized silver nanoparticles with an average size of 35 nm using aqueous leaf extract of *Catharanthus roseus* and proven their activity against malaria parasite. SM Roopana.⁵³ reported the synthesis of silver nanoparticles using *Piper longum* leaf extracts.

The particles had a uniform spherical shape and ranged in size from about 18 to 41 nm. These nanoparticles were found to have a significant cytotoxic effect on HEP-2 cancer cells. In addition to the vast number of reports on angiospermic plants bryophytes are also utilized to synthesise silver nanoparticles. Recently Sougata Ghosh,⁵⁴ reported synthesis of silver nanoparticles using the alcoholic extract of a *Riccia a bryophyte*.

Coconut coir as medium

Gole A.⁵⁵ reported that the reduction of silver ions occurred when silver nitrate solution was treated with aqueous extract of *Cocos nucifera* coir at 60°C, particle synthesised with range of the size as 23±2 nm and face centred cubic silver nanoparticles obtained.

Tuber, rhizome and root extract as medium

Dioscorea bulbifera tuber extract is rich in flavonoid, phenolics, reducing sugars, starch, diosgenin, ascorbic acid, and citric acid.⁵⁶ Energy dispersive x-ray spectroscopy results confirmed the presence of significant amounts of silver with no contaminants and HRTEM images clearly show that the shape of silver nanoparticles were mostly spherical with dimensions of 75 nm. In *Curcuma longa* terpenoids are believed to play an important role in silver nanoparticle biosynthesis through the reduction of silver ions.^{40,57,58} Ag-NPs with an average size of 6.30 ± 2.64 nm and spherical shapes were synthesized using aqueous tuber-powder extract of *C. Longa*.⁵⁹

Bark extract as medium

The compatibility of the bark and powder extracts of *Cinnamon zeylanicum* toward the formation of silver nanoparticles results that bark extract could produce a higher amount of silver nanoparticles compared to the powder extract. The resulting nanoparticles varied in shape and size but had strong antibacterial activity against the *Escherichia coli*.⁶⁰ Savithramma N.⁵⁹ Used bark extracts of *Boswellia ovalifoliolata* and *Shorea tumbuggaia* to synthesise silver nanoparticle.

Seed extract as medium

Joyita Banerjee,⁶⁰ reported the formation of crystalline silver nanoparticles using seed extract of *Syzygium cumuni*. Harekrishna Bar .⁶¹ reported that aqueous seed extract of *Jatropha curcas* can be used for both reducing silver ion to silver and stabilizing the particles during the growth process. They shows that size of the particles can be controlled within certain range from 15-50nm by varying the concentration of AgNO₃. Vijayaraghavan K.⁶² reported synthesis of silver nanoparticles by using seed extract of *Trachyspermum ammi* (ajwain) and *Papaver somniferum*. The extracts of both *T. ammi* and *P. somniferum* showed a maximum absorbance at 430 nm, as the reductant concentration increased the colour intensity also increased .⁶⁰ Audra I Lukman .⁶³ reported that colloidal silver (Ag) nanoparticles were synthesized by reacting aqueous AgNO₃ with *Medicago sativa* seed exudates under non-photomediated conditions. Upon contact, rapid reduction of Ag⁺ ions was observed in <1 min with Ag nanoparticle formation reaching 90% completion in <50 min. Effect of Ag ion concentration, quantity of exudates and pH on the particle size and shape were investigated. At [Ag⁺] = 0.01 M and 30°C, largely spherical nanoparticles with diameters in the range of 5-51 nm were generated, while flower-like particle clusters (mean size = 104 nm) were observed on treatment at higher Ag concentrations.

Flower extract as medium

The synthesis of silver nanoparticles using a broth prepared from the aromatic spath of male inflorescence of screw pine *Pandanus*

odorifer (Forssk).⁶⁴ Flower extract of *Hibiscus sabdariffa* extracellular synthesized silver nanoparticle of 25 nm .⁶⁵

Conclusion

As metal nanoparticles seems to fascinate for the future diverse industry due to their enriched chemical, electrical and physical properties. The development of immaculate protocols for the synthesis of highly monodisperse nanoparticles of various sizes, geometries and chemical composition is one of the most challenging obstructions in the field of nanotechnology. The use of toxic chemicals and non-polar solvents in synthesis leads to the inability to use nanoparticles in clinical fields. Therefore, development of clean, non-toxic, biocompatible and eco-friendly method for synthesis of nanoparticles deserves recognition. So there is need of eco friendly nanoparticles synthesis approach.

Massive numbers of plant species are available in nature, and many of them have huge potential for the production of nanomaterials. For the syntheses of nanoparticles employing plants can be advantageous over other biological entities which can overcome the time consuming process of employing microbes and maintaining their culture which can lose their potential towards synthesis of nanoparticles. And the advantages of using plants for the synthesis of nanoparticles are that the plants are easily available and safe to handle and possess a large variety of active agents that can promote the reduction of silver ions. Most of the plant parts like leaves, roots, latex, bark, stem, and seeds are being used for nanoparticle synthesis. Green synthesis silver nanoparticles using plant extracts provides benefits over chemical and physical method as it is economical, energy efficient, cost effective; provide healthier work places and communities, protecting human health and environment leading to lesser waste and safer products. This eco-friendly method can potentially be used in various areas, including pharmaceuticals, cosmetics, foods, and medical applications. Hence in this regard; use of plant extract for synthesis can form an immense impact in coming decades.

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Conflicts of interest

None.

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