ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Biogenic Synthesis of Metallic Nanoparticles by Plant Extracts

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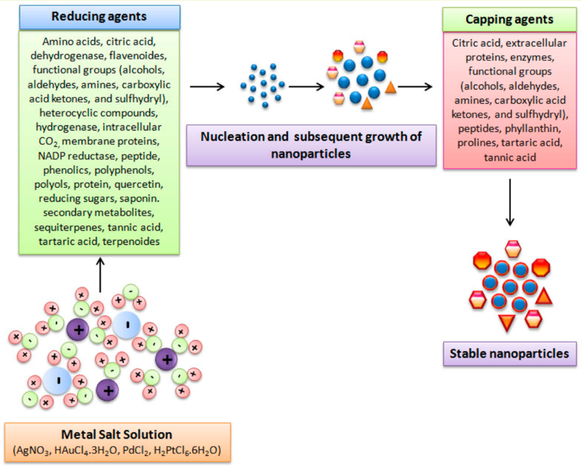
ABSTRACT: In recent years, nanobiotechnology has emerged as an elementary division of modern science and a noval epoch in the fields of material science and is receiving global attention due to its ample applications. Various physical, chemical, and biological methods have been employed to synthesize nanomaterials. Biological systems such as bacteria, fungi, actinomycetes, yeasts, viruses, and plants have been reported to synthesize various metal and metal oxide nanoparticles. Among these, biosynthesis of nanoparticles from plants seems to be a very effective method in developing a rapid, clean, nontoxic, and eco-friendly technology. The use of plant biomass or extracts for the biosynthesis of novel metal nanoparticles (silver, gold, platinum, and palladium) would be more significant if the nanoparticles are synthesized extracellularly and in a controlled manner according to their dispersity of shape and size. Owing to the rich biodiversity of plants, their potential use toward the synthesis of these nobel metal nanoparticles is yet to be explored. The aim of this review is to provide the recent trends involved in the phytosynthesis of nobel metal nanoparticles in the past decade.



KEYWORDS: *Gold, Silver, Platinum, Palladium, Nanoparticles, Phytosynthesis*

INTRODUCTION

Nanobiotechnology represents the intersection of nanotechnology and biotechnology, which is an emerging field dedicated to creation, improvement, and utility of nanoscale structures for advanced biotechnology.[1] An important area of research in this field is the synthesis of nanoparticles with different chemical compositions, sizes, shapes, and controlled dispersities. During the last two decades, the biosynthesis of nobel metal nanoparticles (silver, gold, platinum, and palladium) has received considerable attention due to the growing need to develop environmentally sociable technologies in material synthesis.[2−5] The nanoparticles are of great interest due to their extremely small size and large surface to volume ratio, and they exhibited utterly novel characteristics compared to the large particles of bulk material.[6] Nanoparticles of nobel metals, viz. gold, silver, platinum and palladium, are widely applied in fast-moving consumer goods such as shampoos, soaps, detergents, shoes, cosmetic products, and toothpaste, besides their applications in medical and pharmaceutical products.[7] Gold nanoparticles have been widely used in medicine,[8,9] disease diagnostic and drug delivery systems.[10,11] Silver nanoparticles have been employed in sensor technology,[12] biological leveling,[13] and many other biomedical applications.[14−17] Platinum nanoparticles are also widely used as catalysts[18−20] and in many biomedical applications in combination with other nanoparticles in alloy, core shell, and bimetallic nanostructure.[8,21] Similarly, palladium nanoparticles have an extensive application in catalysis and electrocatalysis,[22−24] sensing, and plasmonic wave guiding.[25,26]

Synthesis of nanoparticles can be performed using a number of routinely used chemical and physical methods. However, altogether these methods are energy and capital intensive, and they employ toxic chemicals and nonpolar solvents in the synthesis procedure and later on synthetic additives or capping agents, thus precluding their applications in clinical and biomedical fields. Therefore, the need for the development of a clean, reliable, biocompatible, benign, and eco-friendly process to synthesize nanoparticles leads to turning researchers toward "green" chemistry and bioprocesses.[27] In recent years, microbial synthesis of nanoparticles has emerged as a promising field of research in nanobiotechnology. Microorganisms such as bacteria, fungi, actinomycetes, yeasts, and viruses are reported to have the innate potential to produce metal nanoparticles either intra- or extra-cellularly and are considered as potential

Received: October 17, 2012
Revised: March 19, 2013
Published: April 1, 2013

Table I. Phytosynthesis of Silver Nanoparticles

plant	part used	nanoparticle type	size	shapes	reference
Aloe vera	leaves	Ag	15.2 nm	spherical	2
Ocimum tenuiflorum	leaves	Ag	25−40 nm	spherical	17
Azadirachta indica	leaves	Ag	–	spherical	47
Pelargonium graveolens	leaves	Ag	16−40 nm	crystalline	54
Emblica officinalis	fruit	Ag	10−20 nm	–	56
Helianthus annus	leaves	Ag	–	–	59
Basella alba	leaves	Ag	–	–	59
Oryza sativa	leaves	Ag	–	–	59
Saccharum officinarum	leaves	Ag	–	–	59
Sorghum bicolour Zea mays	leaves	Ag	–	–	59
Jatropha curcas	latex	Ag	10−20 nm	crystalline	60
Jatropha curcas	seed	Ag	15−50 nm	spherical	61
Carica papaya	fruit	Ag	15 nm	cubic	62
Cinnamon zeylanicum	bark, powder	Ag	31−40 nm	spherical	63
Pinus desiflora	leaves	Ag	15−500 nm	cubic	64
Diopyros kaki	leaves	Ag	15−500 nm	cubic	64
Ginko biloba	leaves	Ag	15−500 nm	cubic	64
Magnolia kobus	leaves	Ag	15−500 nm	cubic	64
Platanus orientalis	leaves	Ag	15−500 nm	cubic	64
Ocimum sanctum	root stem	Ag	5−10 nm	spherical	65
Tanacetum vulgare	fruit	Ag	16 nm	spherical	66
Euphorbia hirta	leaves	Ag	40−50 nm	spherical	67
Argemone maxicana	leaves	Ag	30 nm	cubic, hexagonal	68
Syzygium cumini	leaves	Ag	29−30 nm	spherical	69
Syzygium cumini	seed	Ag	73−92 nm	spherical	69
Sorghum spp.	bran powder	Ag	10 nm	–	70
Curcuma longa	power, tuber	Ag	21−30 nm	quasi-spherical, triangular, rod shaped	71
Allium cepa	leaves	Ag	33.6 nm	spherical	72
Mentha piperita	leaves	Ag	90 nm	spherical	73
Syzygium cumini	seed	Ag	3.5 nm	–	74
Memecylon edule	leaves	Ag	50−90 nm	square	75
Murraya keenigii	leaves	Ag	10 nm	crystalline, spherical	76
Mangifera indica	leaves	Ag	20 nm	spherical, triangular, hexagonal	77
Nicotiana tobaccum	leaves	Ag	8 nm	crystalline	78
Svensonia hyderabadensis	leaves	Ag	45 nm	spherical	79
Citrullus colocynthis	leaves	Ag	31 nm	spherical	80
Boswellia ovalifoliolata	stem bark	Ag	–	spherical	81
Shorea tumbuggaia	stem bark	Ag	–	spherical	81
Cassia auriculata	leaves	Ag	20−40 nm	spherical	82
Zingiber offcinale	rhizome	Ag	6−20 nm	spherical	83
Piper betle	leaves	Ag	3−37 nm	spherical	84
Coleus aromaticus	leaves	Ag	44 nm	spherical	85

biofactories for nanoparticle synthesis.[28] A great deal of effort has been devoted toward the biosynthesis of metal nanoparticles using bacteria,[29−33] fungi,[34−36] actinomycetes,[37−39] yeast,[40] and viruses.[41−43] In addition to the above-mentioned synthesis methods, phytosynthesis that utilizes parts of whole plants as biological factories to synthesize metallic nanoparticles is under exploitation and is an advantageous and profitable approach.[44−46] In comparison to microorganisms, the phytosynthesis method is devoid of complex and multistep processes like microbial isolation, culturing, maintenance etc., and also is a very rapid and cost-effective approach that can be easily scaled up for bulk production of nanoparticles.[47] Moreover, it has been shown that the rate of nanoparticle synthesis is faster using plants than microbes, and the produced nanoparticles are more stable.[46] In addition, phytosynthesis is truly a “green” synthesis route in comparison to other known methods of nanoparticle synthesis. Plants are known to harbor a broad range of metabolites. However, their potential is yet to be fully utilized in full throttle for synthesizing metallic nanoparticles. By using plant tissue culture techniques and optimizing the downstream processing, it is possible to synthesize metal nanoparticles at an industrial scale.[48] The aim of this review is to provide the recent trends involved in phytosynthesis of nobel metal nanoparticles.

■ BIOSYNTHESIS OF NOBEL METAL NANOPARTICLES BY PLANTS

The use of plant systems has been considered a green route and a reliable method for the biosynthesis of nanoparticles owing to its environmental friendly nature.[49,50] It is evident from the earlier reports that plants have been exploited successfully for rapid and extracellular biosynthesis of nobel metal nanoparticles.[7,47,51,52] Shankar et al.[53,54] reported that gold and silver nanoparticles can be synthesized using plant extracts at rates

Table II. Phytosynthesis of Gold Nanoparticles

plant	part used	nanoparticle type	size	shapes	reference
Aloe vera	leaves	Au	–	crystalline	2
Cyymbopogon flexuosus	plant extract	Au	–	spherical, triangular	51
Pelargonium graveolens	leaves	Au	20–40 nm	decahedral, icosahedral	53
Emblica officinalis	fruit	Au	15–25 nm	–	56
Tanacetum vulgare	fruit	Au	11 nm	triangular	66
Menta piperita	leaves	Au	150 nm	spherical	73
Memecylon edule	leaves	Au	10–45 nm	circular, triangular, hexagonal	75
Murraya keenigii	leaves	Au	20 nm	spherical, triangular	76
Cicer arietinum	bean extract	Au	–	triangular	86
Camellia sinensis	leaves	Au	40 nm	spherical, triangular, irregular	87
Coriandum sativum	leaves	Au	6.7–57.9 nm	spherical, triangular turnacated, triangulat, decahedral	88
Eucalyptus camaldulensis	leaves	Au	5.5–7.5 nm	crystalline	89
Pelargonium, roseum	leaves	Au	5.5–7.5 nm	crystalline	89
Azadirachta indica	leaves	Au	5.5–7.5 nm	crystalline	89
Psidium guajava	leaves	Au	25–30 nm	spherical	90
Cinnamomum zeylanicum	leaves	Au	25 nm	spherical, prism	91
Magnolia kobus,	leaves	Au	5–500 nm	spherical, triangle, pentagonal, hexagonal	92
Diopyrus kaki	leaves	Au	5–500 nm	spherical, triangle, pentagonal, hexagonal	92
Terminalia catappa	leaves	Au	10–35 nm	spherical	93
Stevia rebaudiana	leaves	Au	8–20 nm	octahedral	94
Mangifera indica	leaves	Au	17–20 nm	spherical	95
Azadirachta indica	leaves	Au	–	–	96
Beta vulgaris	sugar beet pulp	Au	–	spherical, rod shaped, nanowires	97
Nyctanthes arbortristis	flower extract	Au	19.8 nm	spherical, triangular, hexagonal	98
Cuminum cyminum	seed	Au	1–10 nm	spherical	99
Trigonella foneumgraecum	leaves	Au	15–25 nm	spherical	100
Sphearanthus amaranthoids	leaves	Au	39 nm	spherical	101

Table III. Phytosynthesis of Platinum and Palladium Nanoparticles

plant	part used	nanoparticle type	size	shapes	reference
Gardenia jasminoides	leaves	Pd	3–5 nm	–	4
Doipyros kaki	leaves	Pt	2–12 nm	crystalline	5
Pinus resinosa	bark	Pd	16–20 nm	spherical	24
Pinus resinosa	bark	Pt	6–8 nm	irregular	24
Ocimun sanctum	leaves	Pt	23 nm	irregular	58
Cinnamom zeylanicum	bark	Pd	15–20 nm	crystalline	102
Curcuma longa	tuber	Pd	10–15 nm	spherical	103
Musa paradisica	peeled banana	Pd	50 nm	crystalline irregular	104
Cinnamomum camphora	leaves	Pd	3.2–6.0 nm	–	105
Glycine max	leaves	Pd	15 nm	spherical	106

comparable to those of chemical methods. In a separate study, this group reported the formation of gold nanotriangles when lemongrass leaf extract was allowed to react with aqueous $AuCl_4^-$ ions.[51] In addition, leaf extracts of several plants, viz. lemongrass, neem, tamarind, geranium, and *Aloe vera*, have been reported to demonstrated their potential in reducing Au (III) ions into gold nanoparticles as well as converting silver ions into silver nanoparticles.[2,53,55,56] Similarly, synthesis of platinum and palladium nanoparticles have been reported using extracts of various parts of different plant species.[20,24,57,58] The recent reports on phytosynthesis of nobel metal nanoparticles have been summarized in Tables I–III and are discussed below.

Silver Nanoparticles. Silver has long been recognized for its inhibitory effect toward various microorganisms commonly present in medical and industrial processes.[107] Among biological processes, phytosynthesis of silver nanoparticles has been shown as an easier and more rapid method than the tedious and time-consuming microbial synthesis processes. For instance, parts of plants or their extracts have been explored for the purpose of silver nanoparticle synthesis using silver ions as substrates. Shankar et al.[54] reported the synthesis of highly stable and crystalline silver nanoparticles (16–40 nm) by exposing the aqueous geranium leaf extract to silver nitrate solution. The rate of synthesis of nanoparticles was found to be very high during the reaction (reaction time 60 min). This entails that the use of plants instead of microorganisms for biosynthesis of metal nanoparticles is a more rapid and reproducible process. Later, the same research group reported highly concentrated silver nanoparticles obtained from the aqueous leaf extract of *Azadirachta indica* as well as from the fruit extract of *Embalica officinalis*.[47,56]

Chadran et al.[2] and Li et al.[108] reported the synthesis of silver nanoparticles from the leaf extracts of *Aloe vera* and *Capsicum annum* plants, respectively. Leela et al.[59] performed an interesting experiment using the leaf extracts of plants, namely, *Helianthus annus*, *Basella alba*, *Oryza sativa*, *Saccharum* *officinarum*, *Sorghum bicolar*, and *Zea mays*, and concluded that among all the tested plant extracts, *H. annus* exhibited the strongest potential for rapid reduction of silver ions. Jain et al.[62] demonstrated the rapid synthesis of silver nanoparticles using the fruit extract of *Carica papaya* and found that the synthesized nanoparticles were highly toxic against different multidrug resistant human pathogens. Begum et al.[109] reported rapid synthesis of stable silver nanoparticles of various shapes using black tea leaf extract. Extracellular synthesis of silver nanoparticles has been reported using leaf extract of Pine, Persimmon, Ginkgo, Magnolia, and Platanus plants.[64] In addition, silver nanoparticles were successfully synthesized using the latex and seed extract of *Jatropha curcas*.[61] Dubey et al.[110] reported the use of methanolic extract of *Eucalyptus hybrid* leaves in the extracellular biosynthesis of silver nanoparticles. Similarly, rapid synthesis (reaction time <30 min) of silver nanoparticles using *Acalypha indica* leaf extract and their antibacterial activity against water borne pathogens has been reported by Krishnaraj et al.[111]

Sathiskumar et al.[71] has checked the compatibility of the bark and powder extracts of *Curcuma longa* toward the formation of silver nanoparticles and reported 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*. Similarly, other workers also reported the formation of silver nanoparticles using leaf extract of *Argemone maxicana*,[68] bran powder of *Sorghum* spp.,[70] and leaf extracts of *Allium cepa*[72] and *Euphorbia hirta*.[67] Nabikhan et al.[112] highlighted the possibility of tissue culture-derived callus extract from *Sesuvium portulacastrum* for the synthesis of antimicrobial silver nanoparticles.

Banerjee and Narendhirakannan[74] reported the formation of crystalline silver nanoparticles using seed extract of *Syzygium cumuni*. In addition, Phillips et al.[76] synthesized silver nanoparticles using the leaf extract of *Murraya keenigii*, while Savithramma et al.[81] used bark extracts of *Boswellia ovalifoliolata* and *Shorea tumbuggaia*. Similarly, Udayasoorian et al.[82] also obtained polydispersed and spherical silver nanoparticles using the leaf extract of *Cassia auriculata*, while Satayavani et al.[80] 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, bioinspired synthesis of highly stabilized silver nanoparticles using *Ocimum tenuiflorum* as well as *Coleus aromaticus* have been reported by Patil et al.[17] and Vanaja and Annadurai,[85] respectively. Ponarulselvam et al.[113] synthesized silver nanoparticles with an average size of 35 nm using aqueous leaf extract of *Catharanthus roseus* and proven their activity against malaria parasite. In addition to the vast number of reports on angiospermic plants, recently Kulkarni et al.[114] reported synthesis of silver nanoparticles using the alcoholic extract of a bryophytic plant *Riccia*.

Gold Nanoparticles. Gold nanoparticles are preferably the most attractive member of nobel metal nanoparticles because of their potential applications in the fields ranging from catalysis, nonlinear optics, nanoelectronics, gene expression, and disease diagnosis.[100] Increased environmental concerns over chemical synthesis routs have drawn considerable interest toward phytosynthesis of gold nanoparticles. Shankar et al.[51] reported the formation of gold nanotriangles employing the extract of *Cymbopogon flexuosus*. Similarly, other workers avowed the synthesis of gold nanoparticles using different plant parts such as fruits extract of *Emblica officinale*[56] and leaf extracts of tamarind[55] and *Aloe vera*.[2]

Huang et al.[115] reported the formation of gold nanoparticles from the sun-dried leaves of *Cinnamomum camphora*. The extracellular synthesis of gold nanoparticles using the leaf extract of *Coriandrum sativum* has been attempted by Narayanan and Sakthivel.[88] They found that the synthesized nanoparticles were triangle, truncated, and decahedral in morphology with an average size of 6.7−57.9 nm. Ramezani et al.[89] tested the leaf extracts of three different plants, viz. *Eucalyptus camaldulensis*, *Pelargonium roseum*, and *A. indica*, for the reduction of aqueous chloroaurate solution. The results indicated that all the tested leaf extracts have the ability to produce gold nanoparticles, but a significant increase in the reduction was observed when menthol extracts of *E. camaldulensis* and *P. roseum* were utilized compared to the *A. indica* leaf extract. Raghunandan et al.[90] reported that the addition of microwave-exposed aqueous extracellular guava leaf extract to aqueous gold chloride solution yielded stable poly-shaped gold nanoparticles with high compositions. Ankamwar[93] reported the formation of highly stable gold nanoparticles (10−35 nm) when leaf extract of *Terminalia catappa* was exposed to aqueous chloroaurate solution. Gold nanoparticles of various sizes were also attained by using dried leaf extract of *Stevia rebaudiana*.[94] Moreover, Thirumurugan et al.[96] also successfully produced the gold nanoparticles using the leaf extract of *A. indica*.

Recently, several studies have independently reported the reduction of aqueous cholroaurate solution using various plant parts. The formation of gold nanowires were reported from the pulp extract of *Beta vulgaris*.[97] Similarly, spherical-shaped crystalline gold nanoparticles were synthesized using flower extract of *Nycanthes arbortristis*[98] and leaf extract of *Mangifera indica*.[77]

Very recently, Singh and Bhakat[116] reported the synthesis of gold nanoparticles using leaves and bark of *Ficus carica*. In addition, synthesis of spherical gold nanoparticles have been reported on the reduction of $AuCl_4^-$ by the leaf extract of *Sphearanthus amaranthoids*[101] and *Putranjiva roxburghii*.[117] Synthesis of gold nanoparticles of different sizes in the range of 15−25 nm were obtained by controlling the synthetic parameters using leaf extract of fenugreek.[100]

Platinum and Palladium Nanoparticles. Phytosynthesis of palladium group metal (PGM) nanoparticles has been well reported in recent years.[4,5,102,104] Jia et al.[4] reported the formation of palladium nanoparticles using the aqueous extract of *Gardenia jasminoides* and stated that the antioxidants, namely, geniposide, chlorogenic acid, crocins, and crocetin played very important parts in reducing and stabilizing the nanoparticles whereas the dispersity of these nanoparticles were temperature dependent.

Satishkumar et al.[102] generated palladium nanoparticles with uniform sizes (15−20 nm) using the bark extract of *Cinnamom zeylanicum*. Bankar et al.[104] obtained palladium nanoparticles of 50 nm average size using peeled extract of *Musa paradisica*. In addition, synthesis of platinum nanoparticles was achieved by Song et al.[5] using the leaf extract of *Diopyros kaki*. They reported that more than 90% of the platinum ions were converted into nanoparticles using 10% leaf biomass concentration at 95 °C, and the average size of synthesized nanoparticles ranged from 2 to 12 nm. Furthermore, Yang et al.[105] reported one-pot biogenic fabrication of palladium nanoparticles using leaf broth of *Cinnamomum camphora*.

Phytosynthesis of platinum nanoparticles with controlled shapes and sizes has also been reported by using plant wood nanomaterials.[20]

Recently, Petla et al.[106] synthesized palladium nanoparticles of ~15 nm size using protein-rich soybean leaf extract. Coccia et al.[24] reported one-pot synthesis of platinum and palladium nanoparticles using lignin isolated from red pine (*Pinus resinosa*). Rapid synthesis of platinum nanoparticles has also been reported by Soundarrajan et al.[58] They used leaf extract of *Ocimum sanctum* as a reducing agent for the synthesis of platinum nanoparticles from aqueous chloroplatinic acid.

■ FACTORS AFFECTING PHYTOSYNTHESIS OF METAL NANOPARTICLES

The main challenges frequently encountered in the biosynthesis of nanoparticles are to control the shape and size of the particles as well as to achieve monodispersity in solution phase. There are several factors that may directly influence or cause some hindrance in the phytosynthesis of metal nanoparticles. However, efforts have been devoted to these challenges by controlling the growth factors such as pH, temperature, and reaction or incubation time. In the following section, we have summarized some of the recent reports covering this aspect (Table IV).

Table IV. Effects of Various Factors (pH, Temperature, and Contact or Incubation Time) on the Phytosynthesis of Precious Metal Nanoparticles

factors	shapes	nanoparticles type	reference
pH			
pH 8	spherical, triangular, hexagonal	Ag	77
pH 9	spherical	Au	97
pH 10	rod shaped	Au	97
pH 11	nanowires	Au	97
pH < 5	larger and spherical	Pd	102
pH > 5	smaller and spherical	Pd	102
pH 2	larger and rod shaped	Au	118
pH 3–4	smaller and rod shaped	Au	118
temperature			
25–60 °C	larger and crystalline	Pt	5
25 °C	triangular	Au	92
60 °C	pentagonal	Au	92
90 °C	hexagonal	Au	92
20 °C	larger and spherical	Pd	102
60 °C	smaller and spherical	Pd	102
30 °C	spherical	Pd	103
contact or incubation time			
5 h	spherical	Au	2
25 h	triangular	Au	2
5 h	spherical	Ag	17
11–15 h	spherical and crystalline	Ag	65
10 min	spherical	Ag	66
	triangular	Au	
4 h	cubic and hexagonal	Ag	68
8 h	larger and spherical	Ag	69
24 h	smaller and spherical	Ag	69
24 h	quasi-spherical, triangular, rod shaped	Ag	71
5 h	spherical	Ag	80
10 min	spherical	Ag	81
15 min	spherical	Ag	81
12 h	spherical-triangular, truncated, and decahedral	Au	88
2 min	smaller and spherical	Au	95
5 h	small and spherical	Ag	108
9 h	large and crystalline	Ag	108
11 h	large and polycrystalline	Ag	108
2.5 h	spherical	Au	119
1 h	spherical	Ag	120

Effect of pH. It is obvious from the result of earlier researchers that pH may play a crucial role in the biosynthesis of nanoparticles. Gardea-Torresdey et al.[121] found that pH is an important factor in the biosynthesis of colloidal gold using alfalfa biomass and concluded that the size of nanoparticles varied with the change in pH. Mock et al.[122] also have reached to similar conclusions and reported that pH is responsible for the formation of nanoparticles of various shapes and size. As different plant extracts and even the extracts coming from different parts of the same plant may have different pH values, optimization of a synthetic protocol is needed for efficient synthesis of nanoparticles. It has been reported by several researchers that larger nanoparticles formed at lower pH (2–4) compared to higher pH.[66] Armendariz et al.[118] reported that the size of gold nanoparticles produced by *Avena sativa* was highly dependent on the pH value. At pH 2, large-sized nanoparticles (25–85 nm) were formed, albeit in a small quantity, but at pH 3 and 4, smaller-sized nanoparticles were formed in a large quantity (Table IV). They speculated that at low pH (pH 2), the gold nanoparticles prefer to aggregate to form larger nanoparticles rather than to nucleate and form new nanoparticles. In contrast, at pH 3 and 4, more functional groups (carbonyl and hydroxyl) are available for gold binding; thus, a higher number of new Au (III) complexes would bind to the biomass at the same time that will nucleate separately and form nanoparticles of relatively small size. Similar findings were obtained by Satishkumar et al.[63] who tested the effect of pH during synthesis of silver nanoparticles using *Cinnamom zeylanicum* powder and bark extract over a wider pH range (1–11) and concluded that the pH of the solution dropped in most of the cases after the synthesis of silver nanoparticles. The formation of large-sized ellipsoidal silver nanoparticles was observed at lower or acidic pH, while at higher or alkaline pH, highly dispersed small-sized and spherical nanoparticles tended to form. They also speculated that at higher pH, the availability of a large number of functional groups facilitates a higher number of Ag(I) to bind and subsequently form a large number of nanoparticles with smaller diameter. In addition, Dubey et al.[66] reported that silver nanoparticles demonstrate a lower zeta potential value (−26 mV) at strongly acidic pH compared to alkaline pH solutions, indicating the higher stability and small size of nanoparticles at basic pH. This was also supported by the absorbance peaks in SPR spectra at various pH during their study.

Andreescu et al.[123] reported the rapid and complete reduction of silver at elevated pH and observed a negative zeta potential of the synthesized silver nanoparticles at different pH. They reported that an increase in pH results in an increase of the absolute value of the negative zeta potential, which led to the formation of highly dispersed nanoparticles. This phenomenon could be related to the electrostatic repulsion at high pH or attributed to the high absolute value of the negative zeta potential.[124]

In contrast, Dwivedi and Gopal[125] revealed that silver and gold nanoparticles are stable in a wider range of pH as they observed very small variation in the zeta potential values between pH 2−10 in their study using *Chenopodium album*. Recently, Veerasamy et al.[120] while working on mangosteen leaf extract reported that at low pH aggregation of silver nanoparticles is favored over the nucleation. However, higher pH facilitates the nucleation and subsequent formation of a large number of nanoparticles with smaller diameter.

Effect of Reaction Temperature. It is evidential that the yield of silver nanoparticles has a positive correlation with an increase in temperature.[71] Gericke and Pinches[126] revealed that gold nanoparticles formed with a higher rate at higher temperatures. They observed that nanorod- and platelet-shaped gold nanoparticles were synthesized at higher temperatures, while spherical-shaped nanoparticles formed at lower temperatures. Therefore, the above studies implied that temperature might be one of the crucial factors dominating the size and shape of nanoparticles. Andreescu et al.[123] also reported a rapid synthesis rate of silver nanoparticles at higher temperatures. Lengke et al.[127] described that this phenomenon may occur due to the efficient crystal growth of (1 1 1) faces by the deposition of silver atoms on cubic (1 0 0) faces rather than the nucleation of new silver crystals at elevated temperatures. Additionally, Sathiskumar et al.[71] realized an increase in surface plasmon resonance with an increase in temperature, confirming the positive correlation between the yield of the nanoparticles and the temperature.

Dubey et al.[66] also observed during their study using Tansy (*Tanacetum vulgare*) fruit extract that with an increase in temperature from 25 to 150 °C an increase in the sharpness of absorption peaks was found for both silver and gold nanoparticles. This is so because with an increase in temperature the rate of reaction also increased, which enhances the synthesis of nanoparticles.[125,128] Because the sharpness in absorbance peak depends on the size of the synthesized nanoparticles, as with higher temperature, the particle size may be smaller, which results in the sharpening of the plasmon resonance band of silver and gold nanoparticles.[129,130]

Effect of Contact or Incubation Time. The earlier works also suggested that contact or incubation time also affects the synthesis of nanoparticles. This is the time duration required for completion of all steps of the reaction. Dwivedi and Gopal[125] reported an increase in the sharpness of UV absorption spectra peaks with an increase in contact time while working with *Chenopodium* leaf extract. They reported that nanoparticles appeared within 15 min of the reaction and increased up to 2 h, but after that only slight variation occurred. In a separate study, Dubey et al.[66] observed that in Tansy fruit-mediated synthesis the formation of silver and gold nanoparticles started within 10 min of the reaction. In addition, they found that an increase in contact time is responsible for the sharpening of the peaks in both silver and gold nanoparticles. They also claimed a significant lower contact time requirement in comparison to earlier reports from Fayaz et al.[129] and Shaligram et al.[130] In addition, recently Veerasamy et al.[120] stated that due to the instability of nanoparticles formed an optimum duration is required for complete nucleation and subsequent stability of nanoparticles. This research group observed that the optimum time required for the completion of the reaction for silver nanoparticle synthesis was 60 min during their experiment. Similarly, Ghoreishi et al.[131] also showed the requirement of an optimum reaction time for the stability of synthesized silver and gold nanoparticles using *Rosa damascene*.

■ MECHANISM BEHIND PHYTOSYNTHESIS

While various studies have been commenced on the screening and identification of plants for controlled synthesis of nobel metal nanoparticles, very little work has been performed to understand the actual mechanism behind the synthesis of nanoparticles.[57,71,75] Elucidation of the actual mechanism and biochemical pathways, leading to the biosynthesis of metal nanoparticles, is necessary to develop a rational approach in this field. Research on the underlying molecular mechanism is therefore essential to control the size, shape, and crystallinity of the metal nanoparticles. In recent years, several hypotheses have been proposed for nanoparticles synthesis.[45,132−134] However, the exact mechanism behind the phytosynthesis of metal nanoparticles is not yet known and more detailed studies are needed.[135] In this section, the research works done during the past decade toward elucidating the mechanistic aspect behind the phytosynthesis of metal nanoparticles have been summarized.

After the initial reports published in the 1960s and in the late 1990s,[121,136] many other hypothesis have been proposed toward the phytosynthesis mechanism of metal nanoparticles. In the past decade, the research group at National Chemical Laboratory (NCL), Pune, India has reported their attempts to rationalize the mechanism while synthesizing gold and silver nanoparticles from various plants such as geranium[53,54] neem,[47] lemon grass,[51] tamarind,[55] and chickpea.[137] They reported the presence of proteins and secondary metabolites in the water-soluble fractions of geranium leaves and postulated that terpenoids contributes to the reduction of silver ions and oxidized to carbonyl groups. They have assigned a band of 1748 cm^{-1} to ester C═O group of chlorophyll in FTIR analysis supporting their hypothesis.[53] In another study, protein was found to be involved in the surface capping of gold nanoparticles synthesized using geranium leaf extract.[54] During their attempts to synthesize pure metallic and bimetallic nanoparticles using neem leaf broth, they reported that reducing sugar in the broth could be responsible for the reduction of metal ions and the formation of corresponding metal nanoparticles. The flavanoid and terpenoid constituents of neem leaf broth were believed to be the surface active molecules stabilizing the nanoparticles.[47] While working with the extract of lemon grass (*Cymbopogon flexuosus*), their research group reported the formation of gold nanotriangles due to the reduction of aqueous $AuCl_4^-$ by reducing sugars (aldoses). After reduction, aldehydes/ketones were found to bind with the nascent nanoparticles rendering them "liquid-like" and amenable to sintering at room temperature.[51] The aldehyde/ketones present in the extracts were speculated to play an important role in directing the shape evaluation of gold nanoparticles. In yet another study with tamarind leaf broth, this research group investigated the possibility of an acid group (tartaric acid) to act as a capping agent and to become responsible for the stability of bioreduced gold nanoparticles.[55] In addition, it was reported that CO_2 released during the root growth stage of chickpea seeds (*Cicer arietinum*) may react with aqueous Ca^{2+} ions to produce $CaCO_3$ crystals.[137] The FTIR analysis exhibited the presence of amide I and II peaks, and the gel electrophoresis analysis confirmed the presence of two distinct protein bands of 33 and 39 kDa, which may be responsible for the stabilization of the vaterite $CaCO_3$ structures.[137]

Gardea-Torresdey et al.[138] published their first report on the formation of gold nanoparticles inside living plants. However, the actual mechanism was not elucidated in their report. After one year, this research group reported that alfalfa roots are capable of absorbing silver as Ag (0) from the agar medium and then transfer it to the shoot portion in the same oxidation state.[139] The TEM/STEM analysis in this study suggested that silver atoms accumulated inside the alfalfa plant tissues undergo nucleation and subsequently form nanoparticles. While working with the dead tissues of oats (*Avena sativa*), it was suggested that the functional group such as carbonyl, amino, and sulfhydryl present in the cell wall may also contribute to the reduction of Au (III) to Au nanoparticles.[118]

During the study with *Chilopsis lineasis*, inductive coupled plasmon (ICP) and X-ray diffraction (XRD) spectroscopy were applied to determine the phytoextraction by gold.[140] The authors of this article believed that the ionic form of salt was transported across the root membrane and translocated inside the plant followed by a reduction process to the metal elements. However, details regarding the ion transport were not discussed in this study.

To explain the silver nanoparticle formation from chilli extract, Li et al.[108] proposed a model of "recognition—reduction—limited nucleation and growth". According to this model, in the recognition process, the silver ions are first trapped on the surface of the proteins present in the chilli extract via electrostatic interaction. Thereafter, the silver ions are reduced by these proteins leading to changes in the protein secondary structure and the formation of silver nuclei, which can subsequently grow by further reduction of silver ions, and hence, the resulting elemental silver can accumulate on the preformed nuclei. In this way, the formation of stable spherical silver nanoparticles take place. During the studies on the biogenic formation of silver and gold nanoparticles using *Cinnamomum camphora* leaf extract, Huang et al.[115] reported that polyols were mainly responsible for the reduction of silver and/or chloroaurate ions. Later on, while working with palladium nanoparticles using the same plant, this group reported that heterocyclic components were responsible for the reduction of palladium ions to palladium nanoparticles as well as for their stabilization.[105]

Nadagouda and Varma[57] also reported the green synthesis of silver and palladium nanoparticles using coffee and tea extracts. According to their hypothesis, after the complexation with Ag and Pd metal salts, their reduction into Ag and Pd nanoparticles and capping with oxidized caffeine/polyphenols occur simultaneously. Haverkamp and Marshall[141] reported that plants have limited capacities for reducing the metal ions, and this capacity relies on the reduction potential of metal species. During their work on the uptake of various silver salts solution by hydroponically grown *Barssica juncea*, they proposed that metal nanoparticle formation by plants is restricted to nobel metals. During their study on synthesis of silver nanoparticles using latex of *Jatropha curcas*, Bar et al.[60] reported the involvement of cyclic octa-peptides (Curcacyclin A and B) for the reduction of Ag^+ to Ag nanoparticle and curcain, an enzyme present in the latex of *J. curcus*, for their stabilization. Jha et al.[48] have correlated various physiological and biochemical pathways present in plant systems toward reduction of metal ions into metal nanoparticles during their study using plants of different habitats. In addition to the use of plant extracts, Kasthuri et al.[142] used apiin, a flavonoid glycoside isolated from heena leaves for the synthesis of anistropic Au and quasi-spherical Ag nanoparticles. By using FTIR spectroscopy, they confirmed that the carbonyl group of apiin contributes to the interaction between the nanoparticles and apiin.

On the basis of kinetic studies using FTIR and cyclic voltametry, Begum et al.[109] proposed that polyphenols or flavonoids present in tea leaves were responsible for the Ag and Au nanoparticle synthesis. This group reached to this conclusion as no Ag or Au nanoparticle was observed in the leaf extract lacking polyphenols/flavonoids. Similar results have been reported by Sathishkumar et al.[103] during their study on Pd nanoparticle synthesis using *Curcuma longa* tuber extract. Raghunandan et al.[90] found that flavonoids present in the guava leaf extract were responsible for the synthesis of gold nanoparticles. Song et al.[92] also reported that various plant extracts can be used to synthesize the nobel metallic nanoparticles owing to the existence of terpenoids and reducing sugars in them. During their study on the synthesis of gold nanoparticle with *Magnolia kobus*, they reported that terpenoids having the functional groups of amines, alcohols, ketones, aldehydes, and carboxylic acids were responsible for the stabilization of gold nanoparticles. In a separate study, in contrast to all the other previous reports, this group reported that platinum nanoparticle synthesis using *Diopyros kaki* leaf extract is not an enzyme-mediated process because the rate of nanoparticle synthesis was found to be greatest at the temperature as high as 95 °C, and there were no peaks associated with protein/enzymes on the FTIR analysis.[5]

Dwivedi and Gopal[125] predicted the possible involvement of carbonyl group and carboxylate ions present in *Chenopodium album* leaf extract and their influence on the reduction process and stability of precious metal nanoparticles, respectively. Philip[95] assumed that water-soluble compounds such flavonoids, terpenoids, and thiamine are capping agents for Au nanoparticles. Kumar et al.[69] concluded that the amount of polyphenols present in plant extract could be the crucial parameter determining the size and distribution of synthesized silver nanoparticles.

Very recently, a number of reports have been published on the synthesis of nobel metal nanoparticles from plants with possible mechanism studies.[46,85,100] During the biomimetic synthesis of silver nanoparticles using *Citrus lemon* extract, Prathna et al.[143] demonstrated the ability of citric acid as both the principal reducing agent for the nanoparticle synthesis process and the probable stabilizing agent. Investigations using callus extract of *Citrullus colocynthis* reveled that the compounds attached to the synthesized silver nanoparticles could be polyphenols with aromatic rings and a bound amide region.[80] Interestingly, Narayanan and Sakthivel[144] reported that plant-mediated synthesis could not occurred by enzymes because generally the plant extract is heated to 90 °C during the synthesis process. According to them, phytochemicals such as phenolics, terpenoids, sesquiterpenes, and flavonoids and the functional groups present in these phytochemicals are involved in the reduction and capping of nanoparticles. Similarly, saponins present in the aqueous leaf extract of *Memecylon edule* also contributed to the reduction of silver and gold ions to nanosized silver and gold particles, respectively.[75] Park et al.[133] beautifully reviewed the use of plant-derived polysaccharides and phytochemicals as the reducing and stabilizing agents in the green synthesis of gold and silver nanoparticles. They showed

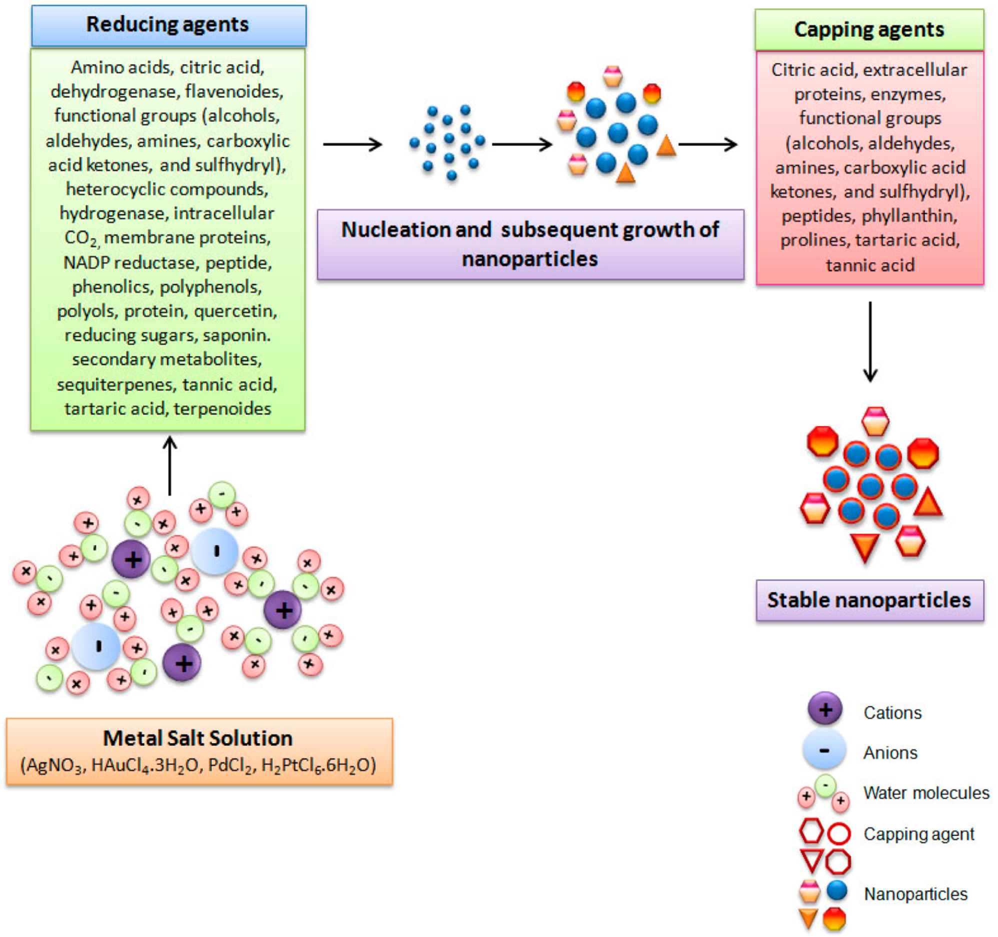


Figure 1. Schematic diagram showing the mechanisms behind the biogenic synthesis of metallic nanoparticles.

that the oxidation of the polysaccharide hydroxyl group in the carbonyl group plays an important role in the reduction of metal salt into nanoparticles. In addition, the reducing end of polysaccharide can also be used to introduce an amino functionality capable of complexing and stabilizing metallic nanoparticles. During the study on *Coleus aromaticus* leaf extract-mediated synthesis of silver nanoparticles, Vanaja and Annadurai[85] speculated that the presence of aromatic amine, amide (I) group, phenolic groups, and secondary alcohols may act as reducing agents for the synthesis of nanoparticles. Armol and Philip[100] reported that fenugreek seed extract has the ability to perform dual function of reduction and stabilization of gold nanoparticles. They elaborated that flavonoids present in seed extract are powerful reducing agents that may be responsible for the reduction of chloroauric acid, whereas the carboxylate group present in proteins can act as a surfactant to attach onto the surface of gold nanoparticles and stabilize them through electrostatic stabilization. After critically reviewing all the proposed mechanisms so far, we have developed a pictorial diagram depicting the possible mechanisms behind phytosynthesis of nobel metal nanoparticles (Figure 1).

CONCLUSIONS

This review has summarized the recent research work in the field of phytosynthesis of nobel metal nanoparticles and critically discusses the various mechanisms proposed behind it. Owing to the rich biodiversity of plants, their potential for the synthesis of nobel metal nanoparticles is yet to be fully explored. Massive numbers of plant species are available in nature, and many of them can be excellent candidates for nanoparticle synthesis. Elucidation of mechanism behind phytosynthesis of precious metal nanoparticles is necessary in order to develop a rational approach. A thorough understanding of biochemical mechanisms involved in the plant-mediated nanoparticle synthesis is a prerequisite in order to make this approach economically competitive with the conventional methods. However, it is intimidating due to the complexity and vast variability in different plant systems. Although many reports have been published with a proposed mechanism, almost all of them are just reasonable hypotheses without any convincing experimental support. Because the hypotheses also vary with various plant species, further in depth evaluation is therefore necessary in order to understand the actual mechanism of a particular plant system. Therefore, this still remains an important issue.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors (M.S.A. and Y.S.Y.) are highly grateful for the financial support from World Class University (WCU) fellowship program at Environmental Biotechnology National research laboratory (EBTL), Department of BIN Fusion Technology, Chonbuk, National University, Republic of Korea. The Second author (J.P.) is thankful to World Bank Indian Council of Agricultural Research funded NAIP project for financial assistance.

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