Green Synthesis of Plasmonic Metal Nanoparticles and Their Application as Enviromental Sensors

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Contents

Abbreviations

AgNPs	Silver nanoparticles
AuNPs	Gold nanoparticles
FTIR	Fourier transform infrared spectroscopy
GSH	Glutathione
LSPR	Localized surface plasmon resonance
NADH	Nicotinamide adenine dinucleotide
SERS	Surface-enhanced Raman spectroscopy

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1 Introduction

Plasmonic metal nanoparticles have drawn wide attention due to their unique optical properties, size, and shape-dependent properties and tunable optical response over a spectral range from visible to the near-infrared region (Rao et al. 2002; Tao et al. 2008). Among metal nanoparticles, silver and gold nanoparticles (AgNPs and AuNPs) exhibit unique optical features and strong significant absorption in the visible region. This behavior refers to a collective oscillation of the surface conduction electrons. The collective oscillation of the surface conduction electrons is called surface plasmons. The resonance of surface plasmons with certain frequencies of incident electromagnetic radiation of light is known as localized surface plasmon resonance (LSPR) (Willets and Van Duyne 2007; Mayer and Hafner 2011). These extraordinary properties have made plasmonic metal nanoparticles considerable interest and fantastic nanoscale platform in biological and chemical sensing approaches in the area of food safety (Homola 2004; Narsaiah et al. 2012), disease diagnosis (Barizuddin et al. 2016), and environmental analysis (Wei et al. 2015).

High-quality plasmonic metal nanoparticles can be fabricated by various physical and chemical synthetic methods (Nisbet and Weiss 2010). Besides, green and biosynthesis routes as alternatives to the conventional physical and chemical synthesis strategies offer clean, nontoxic, and environmentally friendly synthetic approaches for the large-scale, more feasible, cost-effective, and faster production of metal nanoparticles (Gahlawat and Choudhury 2019). By utilizing green synthesis techniques biocompatible nanoparticles are produced by natural agents (Babu et al. 2013). The green synthesis methods do not require expensive, toxic, and harmful chemical reagents. Therefore, green synthesis results in eliminating using toxic chemicals. Also, green synthesis can significantly reduce environmental contamination and harmful residues. These advantages make the produced nanoparticles safe for both therapeutic uses and environment (Abdeen et al. 2014). Moreover, biosynthesis of nanoparticles using the natural, pure, and green substances is mostly carried out at room temperature (Gao et al. 2014). Therefore, this synthetic strategy has other several advantages over the traditional chemical methods due to low energy consumption and moderate operation condition. Owing to these advantages, the green synthesis of nanoparticles has gained significant attention in recent years.

Green synthesis approaches using various microorganisms such as yeasts, molds, fungi, algae, and bacteria, and plants due to their natural bioactive molecules including proteins, enzymes, amino acids, polysaccharides, phenolic compounds, amines, alkaloids, vitamins, and pigments have been developed for eco-friendly synthesis of metal nanoparticles (Adil et al. 2015; Gahlawat and Choudhury 2019; Ahmad et al. 2019; Hulkoti and Taranath 2014). Most of these viable natural biomolecules can be used as reducing agents, stabilizers, or both. The bioactive molecules can bind to metal ions through their functional groups such as hydroxyl and carbonyl . Then these biomolecules can fabricate nanoparticles and also prevent the aggregation of nanoparticles (Duan et al. 2015; Mohammadlou et al. 2016). Figure 1 illustrates a graphical green synthetic route of metal nanoparticles from the extract of microor-

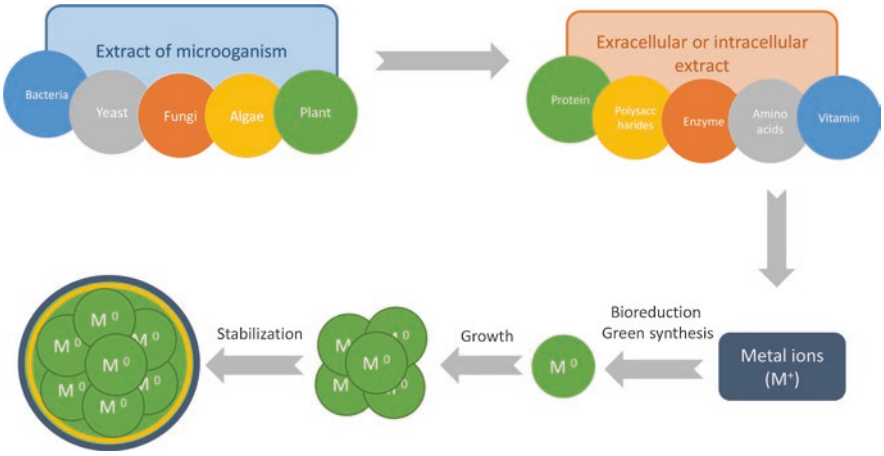

Fig. 1 Graphical representation of green synthesis of metal nanoparticles using microorganisms and plant extracts and mechanism of metal nanoparticle formation

ganisms. Different green synthesis methods of metal nanoparticles are classified into the mentioned categories which are described in more detail in the following sections.

Depending on the area where nanoparticles are generated, the biosynthesis may occur either intracellular or extracellular. The exact mechanism of biosynthesis of metal nanoparticles using bioreagents is not very clear yet. Different microorganisms and different biomolecules have displayed different pathways for the formation of metal nanoparticles. However, in most of biosynthetic routes metal ions get trapped on the surface of microbial cell walls or diffuse inside the cells and then further get reduced to metal nanoparticles via an enzymatic or nonenzymatic method (Ali et al. 2019). In intracellular synthesis process, positively charged metal ions get attracted to the negatively charged cell wall based on electrostatic interaction between metal ions and the cell wall. Entrapped metal ions could be reduced to metal nanoparticles due to the presence of enzymes on the cell wall. Then the produced nanoparticles get diffused off through the cell wall (Hulkoti and Taranath 2014). In extracellular synthesis methods, nitrate reductase enzyme is mostly responsible for bioreduction of metal ions (Hulkoti and Taranath 2014). The nitrate reductase enzyme which is involved in the cellular nitrogen cycle is able to reduce nitrate to nitrite. In several studies on the mechanism of extracellular biofabrication of nanoparticle, it was revealed that nicotinamide adenine dinucleotide (NADH)-dependent nitrate reductase enzyme is capable to reduce metal ions to metal nanoparticles via an electron transfer process, followed by metal nanoparticle formation and stabilization (Shah et al. 2015). Indeed, NADH provides required electrons for reductase enzyme and is then oxidized to NAD^+. During the electron transfer from NADH to nitrate-dependent reductase, each metal ion receives an electron and gets reduced to a metal atom (Waghmare et al. 2014).

2 Green Synthesis of Silver and Gold Nanoparticles Using Different Microorganisms

2.1 Synthesis of Silver and Gold Nanoparticles Using Bacteria

Generally, different parameters such as pH, temperature, metallic salt, and culturing media can significantly influence on size, shape, and properties of produced nanoparticles during bacterial-mediated synthesis methods. Also, the selection of an appropriate culturing method is very important. Because the culturing condition like pH, temperature, light, nutrients, and buffer strength can result to increase enzyme activity and subsequently lead to an increase the particle yield (Shah et al. 2015).

By considering synthesis condition, some bacterial strains such as *Actinobacter* sp. (Wadhwani et al. 2016), *Escherichia coli* (Srivastava et al. 2013), *Klebsiella pneumonia* (Prema et al. 2016), *Lactobacillus casei* (Kato et al. 2019), *Bacillus methylotrophicus* (Wang et al. 2016a), *Corynebacterium glutamicum* (Gowramma et al. 2015), and *Pseudomonas* sp. (Klaus et al. 1999) have been reported as potential biofactories for production of silver and gold nanoparticles either intracellularly or extracellularly. *Pseudomonas stutzeri AG259* has been applied for intracellular biosynthesis of triangles and hexagonal silver nanocrystals up to 200 nm (Klaus et al. 1999). *Pseudomonas mandelii* was used for fabrication of highly stable AgNPs with small diameter of 1.9–10 nm under low temperature conditions (Mageswari et al. 2015). Spherical AgNPs with the size of 5–50 nm were obtained from alkaliphilic actinobacterium *Nocardiopsis valliformis* (Rathod et al. 2016). Green synthesis of Ag and AuNPs and Au–Ag alloy crystal was assisted by *Lactobacillus* which is present in buttermilk (Nair and Pradeep 2002). Biosynthesis of 15 nm AgNPs has been achieved using native isolates of *Corynebacterium glutamicum* (Gowramma et al. 2015). *Acinetobacter* sp. SW30 (Wadhwani et al. 2016), *Bacillus methylotrophicus* DC3 (Wang et al. 2016a), and *Bacillus licheniformis* M09 supernatant (Momin et al. 2019) were used for biosynthesis of AgNPs with antimicrobial activity and a mean size of 19 nm, 10–30 nm, and 10–30 nm, respectively.

AuNPs were synthesized with the average size of 22.2 nm using cell extracts of *Labrys* sp. (Shen et al. 2018). pH-dependent extracellular biosynthesis of AuNPs with different sizes and shapes was reported using *Rhodopseudomonas capsulata*. Spherical AuNPs in the size range of 10–20 nm were formed at pH 7 while some nanoplates were obtained at pH 4 (He et al. 2007). Also in another study, cell free extract of *Rhodopseudomonas capsulata* was used for the synthesis of gold nanowires with the size of 10–20 nm. It was elucidated that proteins were responsible for gold nanowire formation (He et al. 2008). Also, another bacterium, *Stenotrophomonas maltophilia* synthesized well-dispersed AuNPs with an average diameter of 40 nm (Nangia et al. 2009). Circular AuNPs with the average size of 50 nm were obtained at room temperature using *Escherichia coli* K12. It was revealed that some peptides in the membrane of *Escherichia coli* K12 were involved

in synthesis and stabilization of AuNPs (Srivastava et al. 2013). *Geobacillus* sp. strain ID17 was also used for biosynthesis of spherical AuNPs with the size of 5–50 nm. Also, quasi-hexagonal AuNPs with the size between 10 and 20 nm were obtained using *Geobacillus* sp. strain ID17 (Correa-Llantén et al. 2013). Microbial biosynthesis of AuNPs was evaluated using *Klebsiella pneumonia*. The extract of *Klebsiella pneumonia* yielded to the formation of spherical AuNPs with the size between 10 and 15 nm (Prema et al. 2016). In another study, glycolipids present in the cell membrane of *Lactobacillus casei* were involved in bioreducing gold ions into AuNPs (Kato et al. 2019).

2.2 Synthesis of Silver and Gold Nanoparticles Using Yeast

All yeast genera are capable of accumulation of different heavy metals. Cell membrane transportation of metals is controlled by enzymatic oxidation or reduction, chelating with extracellular polysaccharides and peptides, and sorption at the cell wall. The yeast species are known as "semiconductor crystals" or "quantum semiconductor crystals" because of their strong potential in the synthesis of semiconductor nanoparticles (Dameron et al. 1989). However, they can also produce other nanoparticles including metal nanoparticles. Spherical silver nanoparticles with the size of 6–20 nm were obtained using *Saccharomyces cerevisiae* as a bioreducing agent (Jha and Prasad 2008). AgNPs were synthesized on the yeast cells *Saccharomyces cerevisiae* BU-MBT-CY1 isolated from coconut cell sap, with an average diameter of 19 ± 9 nm. The prepared AgNPs were applied for As (V) removal (Selvakumar et al. 2011). Green and rapid synthesis of highly stable AgNPs with the size of 3–10 nm was reported using cell free extract of *Saccharomyces boulardii*. It was elucidated that proteins and peptides of this yeast were involved in the formation and stabilization of AgNPs. The obtained AgNPs exhibited anticancerous activity (Kaler et al. 2013). Also, the culture extract of *Rhodotorula* sp. was appeared as a novel biocatalyst for bioreduction of silver ions to AgNPs with an average size of 40 nm (Ashengroph 2014). The psychrotrophic marine yeast *Yarrowia lipolytica* containing brown pigment (melanin) synthesized AgNPs, and the obtained AgNPs were used as antibiofilm agents (Apte et al. 2013). Proteins present in marine yeast *Candida* sp. were used as a bioreducing agent for producing AgNPs with antimicrobial activity (Kumar et al. 2011). Yeast *Trichosporon montevideense* was used for biosynthesis of AuNPs (Shen et al. 2018). Spherical AuNPs with the size below 100 nm were generated using *Pichia jadini* (Gericke and Pinches 2006). Also, both intracellularly (Pimprikar et al. 2009) and extracellularly (Agnihotri et al. 2009) biosynthesis of AuNPs have been reported using marine yeast *Yarrowia lipolytica* (*Candida lipolytica*).

2.3 Synthesis of Metal Nanoparticles Using Fungi

Most of the fungal genera contain a high amount of proteins and enzymes. Therefore, fungi are biosynthetic productive agents for green synthesis of metal nanoparticles. In addition, they have high intracellular metal uptake capacity, high binding, and metal bioaccumulation capacity and specific enzymes such as reductase. The existence of these enzymes facilitates the biosynthesis of metal nanoparticles (Hulkoti and Taranath 2014). Using fungi in the synthesis process, highly monodisperse nanoparticles can be produced. Based on reports, different fungi have been evaluated for the production of metal nanoparticles. In this regard, stable 5–15 nm AgNPs were synthesized using *Fusarium oxysporum* (Ahmad et al. 2003). The fungus *Pestalotiopsis pauciseta* was used for biological synthesis of AgNPs with the size of 123–195 nm (Vardhana and Kathiravan 2015). Spherical AgNPs with the average diameter of 12–20 nm were produced biologically using the endophytic fungus *Fusarium* sp. (Singh et al. 2015). Fast and simple extracellular synthesis of AgNPs was carried out using fungal biomass of *Aspergillus fumigatus* and the obtained AgNPs were in the range of 5–25 nm (Bhainsa and D'souza 2006). In one study, biosynthesis of AgNPs using three endophytic fungi *Aspergillus tamarii* PFL2, *Aspergillus niger* PFR6, and *Penicillium ochrochloron* PFR8 were considered and the size of obtained nanoparticles was compared. According to observations, using the fungi *A. tamarii* PFL2 smaller particle size (3.5 ± 3 nm) was obtained compared to the generated AgNPs by the other two fungi (Devi and Joshi 2015). *Arthroderma fulvum* HT77 was employed for biosynthesis of antifungal AgNPs with the average diameter of 15.5 nm (Xue et al. 2016). Also, biosynthesis of AgNPs was investigated using four different fungal species such as *Rhizopus nigricans*, *Fusarium semitectum*, *Colletotrichum gloeosporioides*, and *Aspergillus nidulans* (Ravindra and Rajasab 2014). Biofabrication of AgNPs was studied using an endophytic fungus identified as *Botryosphaeria rhodina* which was secreted from the medicinal plant *Catharanthus roseus* (Linn.) (Akther et al. 2019).

Using *Fusarium acuminatum* MTCC-1983, AuNPs were obtained with the size of 17 nm via enzymes secreted by the fungus (Tidke et al. 2014). Moreover, different shapes of AuNPs were synthesized with various fungi. Triangle, pentagon, and hexagon-shaped AuNPs with the average size of 10–60 nm were produced using cells and biomass of *Aspergillus oryzae var. viridis* (Binupriya et al. 2010). Biomass of *Trichothecium* spp. *Link*. synthesized triangle and hexagonal AuNPs with the size in the range of 5–200 nm under stationary or shaking conditions which caused extracellular and intracellular formation of nanoparticles, respectively (Ahmad et al. 2005). Spherical and triangular AuNPs were synthesized using *Fusarium oxysporum* in the size range of 20–40 nm (Mukherjee et al. 2002). Gold nanocrystals with the mean size of 10 nm were biofabricated using *Rhizopus oryzae*. The gold nanocrystals were synthesized on the surface of *Rhizopus oryzae* cell (Das et al. 2009). *Fusarium oxysporum* was also used for generation of highly stable Au–Ag alloy with a diameter between 8 and 14 nm (Senapati et al. 2005). Ag-Au alloy was

obtained using fungal xylanases extracted from *Aspergillus niger* L3 and *Trichoderma longibrachiatum* L2. Biosynthesized alloy nanoparticles displayed potential biomedical applications (Elegbede et al. 2019).

2.4 Synthesis of Silver and Gold Nanoparticles Using Algae

Metal nanoparticles can be fabricated using algae which are known as a source of biomaterials such as proteins, amino acids, carbohydrates, pigments, fatty acids, and nucleic acids. Several algae have been employed for green synthesis of silver and gold nanoparticles. Extracellular biosynthesis of AgNPs was evaluated using a brown seaweed *Sargassum wightii*. The obtained AgNPs displayed antibacterial activity (Govindaraju et al. 2009). Also, the edible blue green alga *Spirulina platensis* was studied for extracellular synthesis of biocompatible AgNPs (Govindaraju et al. 2009). In one study, different strains of microalgae such as *Botryococcus braunii, Coelastrum* sp., *Spirulina* sp., and *Limnothix* sp. produced AgNPs with the size of about 13–25 nm. Also, different shapes of AgNPs such as spherical, elongated, and irregular nanoparticles were synthesized. Based on the obtained data it was indicated that polysaccharides found in extracellular cell-free cultural liquid of algae and protein-based pigments of cyanobacteria were involved in nanoparticle formation (Patel et al. 2015). The biosynthesis of antibacterial AgNPs was assisted using the aqueous extract of the red marine macroalga *Amphiroa fragilissima*. Also, AgNPs with antibacterial activity were synthesized via marine alga *Caulerpa racemosa* (Kathiraven et al. 2015). In one report, an aqueous extract of *Chlorella vulgaris* proved to be suitable for the biosynthesis of AgNPs with the size range of 15–47 nm (Annamalai and Nallamuthu 2016). The synthesis of spherical AgNPs was carried out using *Ulva fasciata* extract as a reducing and capping agent (Rajesh et al. 2012). Recently, it was reported that the green alga *Botryococcus braunii* was used for the synthesis of spherical, cubic and truncated triangular AgNPs with the size of 40–90 nm. The synthesized AgNPs exhibited catalytic activity in the conversion of 2-nitroaniline to biologically important 2-arylbenzimidazoles. According to the FTIR spectrum, it was revealed that bioactive molecules such as proteins, amides, polysaccharides, and long chain fatty acids found in *Botryococcus braunii* extract were responsible for the synthesis and stabilizing of AgNPs (Arya et al. 2019). Another green alga, *Chlorella vulgaris*, resulted in the biosynthesis of AgNPs. Based on FTIR obtained spectrum, it was revealed that polysaccharides, amides, proteins, and chain fatty acids of *Chlorella vulgaris* are responsible for AgNPs formation. Green synthesis using *Chlorella vulgaris* yielded triangular AgNPs in the range of 40–90 nm (Mahajan et al. 2019). The whole-cell aqueous extract of *Neochloris oleoabundans* was employed for the synthesis of quasi-spherical AgNPs with a mean diameter of 16.63 nm under light (Bao et al. 2019). A sulfated polysaccharide present in the extract of the green alga *Ulva armoricana* appeared to be a reducing and stabilizing agent for synthesis of AgNPs with a thick polysaccharide shell. The synthesis was carried out under mild conditions (Massironi et al. 2019).

The marine alga *Sargassum wightii* has been applied for the biological formation of stable AuNPs with the size of 8–12 nm (Singaravelu et al. 2007). In one report, AuNPs were produced by blue green algae with antibacterial activity (Suganya et al. 2015). The biomass of a green microalga, *Chlorella vulgaris*, was used for the synthesis of gold nanoplates (Dahoumane et al. 2017). Highly stable small AuNPs with a mean diameter of 5.42 nm were yielded using brown marine macroalga *Sargassum muticum.* Moreover, the aqueous extract of *S. muticum* appeared to act as both reducing and stabilizing agent (Namvar et al. 2015). The brown alga *Cystoseira baccata* was employed for the biosynthesis of AuNPs with the size of 8.4 nm and cytotoxic activity against colon cancer cells (González-Ballesteros et al. 2017). In another study, green synthesis of AuNPs with the size of 15 and 47 nm was considered using the green alga *Chlorella vulgaris* (Annamalai and Nallamuthu 2016). Marine red seaweed *Gracilaria verrucosa* was applied for facile one-pot synthesis of biocompatible AuNPs with the size range of 20–80 nm. Different isotropic and anisotropic AuNPs such as spherical, oval, triangular, octahedral, pentagonal, and rhomboid nanoparticles were obtained. Proteins, phenolic and aromatic compounds of the studied seaweed were responsible for the synthesis of AuNPs (Chellapandian et al. 2019). The extract of the red marine alga *Gelidiella acerosa* fabricated spherical and hexagonal AuNPs with antibacterial, antioxidant, and antidiabetic activity. The particle size of the synthesized AuNPs was estimated in the range of 5.81–117.59 nm. Terpenoids, cardiac glycosides, alkaloids, and tannins present in *Gracilaria verrucosa* extract acted as bioreducing and capping agent (Senthilkumar et al. 2019). Aqueous extracts of two marine brown algae, *Turbinaria conoides* and *Sargassum tenerrimum*, were used as both reducing and capping agent for green synthesis of spherical AuNPs with the size of 27–35 nm. It appeared that the brown alga *T. conoides* is rich in polysaccharides, sulfated polysaccharides, and polyphenolic compounds and *S. tenerrimum* extract is containing various secondary metabolites such as proteins, amino acids, carbohydrates, phenolic acids, sterols, alkaloids, flavonoids, and tannins. These biomolecules can act as reducing as well as stabilizing agents. The biosynthesized nanoparticles using the applied brown algae exhibited catalytic activity (Ramakrishna et al. 2016).

Au and Ag nanoparticles were biosynthesized using the red seaweed *Chondrus crispus* and the green alga *Spirogyra insignia* as reducing agents. *C. crispus* is containing sulfated polysaccharides which are able to bind to gold nanoparticles surface and stabilize the produced AuNPs. Using *C. crispus* at different pH, AuNPs with different shapes were obtained. In acidic media (pH 2) mostly triangle and hexagonal AuNPs were produced and at pH 4 spherical nanoparticles with the average size of 30 nm were formed. Also, *Spirogyra insignia* is containing pectins which are polysaccharides rich in galacturonic acid. There are huge amount of hydroxyl, ketone, aldehyde and carboxylic acid groups in the structure of these biomolecules which are appeared as reducing and capping agent in synthesis of AgNPs (Castro et al. 2013). Also, it has been reported that a red alga, *Gracilaria* sp., was used for the extracellular biosynthesis of Au, Ag, and Au/Ag bimetallic nanoparticles with antibacterial activity (Ramakritinan et al. 2013). Some related studies on algae-mediated synthesis of Ag and AuNPs last recent years are summarized in Table 1.

Table 1 Algae-assisted synthesis of silver and gold nanoparticles

Algae	Biomolecules	Metal nanoparticle	Size and shape	Ref
Green microalgae				
Botryococcus braunii	Proteins, amides, polysaccharides, and long chain fatty acids	Ag	40–90 nm, spherical, cubic, truncated, triangular	Arya et al. (2019)
Chlorella vulgaris	Protein	Ag	5–50 nm	Annamalai and Nallamuthu (2016)
Caulerpa serrulata	Caulerpenyne and/or its derivatives	Ag	10 ± 2 nm, spherical	Aboelfetoh et al. (2017)
Rhizoclonium fontinale	Chlorophyll, protein, and carbohydrate	Au	pH 5: 5–20 nm spherical, 15–88 nm, nanotriangles 34 nm, nanohexagons, rod-shaped (~100 × 51.5 nm); pH 7: Spherical 13–22 nm, pH 9: 16 nm, nanospheres	Parial and Pal (2015)
Brown microalgae				
Sargassum vulgare	Alginate moieties, secondary OH groups	Ag	10 nm, spherical	Govindaraju et al. (2015)
Padina pavonia	Protein Polysaccharides	Ag	49.58–86.37 nm, spherical, triangular, rectangle, polyhedral and hexagonal	Abdel-Raouf et al. (2018)
Cystoseira baccata	Polyphenols Polysaccharides	Au	8.4 ± 2.2 nm, spherical	González-Ballesteros et al. (2017)
Sargassum tenerrimum	Amino acids Alkaloids Carbohydrates Flavonoids Saponins Sterols Tannins Proteins Phenolic acids	Au	5–45 nm, anisotropic	Ramakrishna et al. (2016)
Red microalgae				
Acanthophora specifera	Monosaccharide, polysaccharide, uronic acids and secondary metabolites	Ag	33–81 nm, cubic	Ibraheem et al. (2016)
Portieria hornemannii	Protein Phenolic compounds	Ag	9–80 nm, spherical	Ramamoorthy et al. (2019)

(continued)

Table 1 (continued)

Algae	Biomolecules	Metal nanoparticle	Size and shape	Ref
Gracilaria verrucosa	Protein Phenolic and aromatic compounds	Au	20–80 nm, as spherical, oval, triangular, octahedral, pentagonal and rhombus shapes	Chellapandian et al. (2019)
Galaxaura elongata	Palmitic acid Polyphenolic compounds	Au	3.85–77.13 nm, rod, triangular, truncated, triangular, hexagonal	Abdel-Raouf et al. (2017)

2.5 Synthesis of Metal Nanoparticles Using Plants

Plant-based synthesis method has attracted much more attention rather than the other green agents because it provides rapid single step synthesis process. Green synthesis of metal nanoparticles using reactive plant derivative reagents and phytochemicals has been greatly popularized nowadays. The extracts of different parts of plants like leaves, roots, stems, bark, pods, peel, seeds, flowers, and fruits have been used as reducing reagent for the synthesis of metal nanoparticles (Iravani 2011; Gour and Jain 2019). Phytochemicals present in the plant extracts such as polysaccharides, polyol and heterocyclic compounds, essential oils, sugar, flavonoids, proteins, enzymes, alkaloids, tannins, terpenoids, vitamins, and organic acids are mainly responsible for the bioreduction of metal ions into metal nanoparticles and also can act as a capping agent of the fabricated nanoparticles (Iravani 2011; Makarov et al. 2014). For instance, terpenoids are a group of organic polymers with strong antioxidant activity and are able to reduce metal ions. Flavonoids are polyphenolic compounds with various functional groups which are capable to actively chelate to metal ions and reduce them to form nanoparticles. Moreover, sugar, monosaccharides like glucose, disaccharides, and polysaccharides can act as reducing agents due to their active sites, free aldehyde groups, and their type and concentrations (Makarov et al. 2014). In comparison with using microorganisms for the synthesis of nanoparticles, plant-based synthesis is more rapid and has some advantages over microorganisms. Plants have a large range of active reagents. Plant extracts do not need to complex treatment process like isolation, culturing and maintenance. Plants are easily accessible and due to having great potential in detoxification and heavy metal accumulation are more appropriate candidates for the biosynthesis of metal nanoparticles. Also, more stable nanoparticles are produced using plant extracts. Moreover, size and morphology controlled nanoparticles can be obtained considerably more feasible when plant extracts were used for biosynthesis of metal nanoparticles (Mohammadlou et al. 2016; Iravani 2011; Shah et al. 2015; Jha et al. 2009). Several affecting parameters including type of plant and phytochemicals, concentration of metal ions and extracts, time, pH and temperature are the key factors on the metal nanoparticles generation and also can influence on the size and morphology of the produced nanoparticles (Shah et al. 2015).

It has been reported that different parts of plants have been employed for the biosynthesis of metal nanoparticles. For instance, in some studies the leaf extract of *Geranium* (Rivera-Rangel et al. 2018; Shankar et al. 2003), *Helianthus annuus, Basella alba,* and *Saccharum officinarum* (Leela and Vivekanandan 2008), *Glycine max* (soybean) (Vivekanandhan et al. 2009), *Syzygium cumini* (Kumar et al. 2010), *Coriandrum sativum* (Khan et al. 2018a), *Pinus densiflora* (Basiri et al. 2018), and *Casuarina equisetifolia L.* (Muthu and Rathika 2016) have appeared suitable for bioreduction and biosynthesis of AgNPs with different sizes. Green synthesis of AgNPs using banana peel extract has been demonstrated. The banana peel extract was used as both reducing and capping agent (Ibrahim 2015). Moreover, ethanolic extract of rose petals (*Rosa indica*) (Manikandan et al. 2015), aqueous seed extract of *Pistacia atlantica* (Sadeghi et al. 2015), aqueous stem bark extract of *Syzygium alternifolium* (Yugandhar et al. 2015), and fruit extracts like kiwi fruit juice (Gao et al. 2014), blackberry (Kumar et al. 2017a), *Cucumis melo* (Basiri et al. 2017), and lingonberry and cranberry juices (Puišo et al. 2014) were evaluated for synthesis of AgNPs.

The root extract of *Cucurbita pepo* L. was used for bio-catalyzed synthesis of AuNPs (Gonnelli et al. 2015). Also, *Cucurbita pepo* L. leaf extract was applied for fabrication of morphology controlled AuNPs (Gonnelli et al. 2018). Using mango peel extract, AuNPs in particle size of 6–18 nm were obtained at pH 9 and 2 (Yang et al. 2014). Leaf extract of *Sesbania grandiflora* was led to the formation of well-dispersed 7–34 nm AuNPs (Das and Velusamy 2014). Phytochemical compounds present in the seed, skin, and stalk of grape such as catechin, epicatechin, anthocyanidin, proanthocyanidin, and condensed tannins were able to produce stabilized AuNPs with the average size of 20 nm (Krishnaswamy et al. 2014). In another study, it was revealed that carbohydrates, tannins, flavonoids, and phenolic acids present in the fruit of *Phoenix dactylifera* (date palm) were responsible for the formation and stabilization of spherical AuNPs in the size range of 32–45 nm (Zayed and Eisa 2014).

Several plant extracts such as seed extract of *Madhuca longifolia* (Sharma et al. 2019), leaf extract of gold rod (*Solidago canadensis*) (Botha et al. 2019) and *Stigmaphyllon ovatum* (Elemike et al. 2019) have been used for green synthesis of both Ag and Au nanoparticles and also bimetallic Ag/AuNPs. Also, the extract of medicinal plants including the root extract of ginger (*Zingiber officinale*) (Velmurugan et al. 2014) and leaf extract of *Cinnamomum camphora* (Huang et al. 2007) have been evaluated for synthesis of both Ag and AuNPs. In one study, Ag and AuNPs were synthesized using the extract of blueberry, blackberry, turmeric, and pomegranate. In this study, more uniform metal nanoparticles were obtained using pomegranate extract (Nadagouda et al. 2014).

Different morphologies of silver and gold nanoparticles have been fabricated by plant extracts. The extract of *Aloe vera* have been utilized for biofabrication of triangular AuNPs and spherical AgNPs (Chandran et al. 2006) and also octahedron AgNPs (Logaranjan et al. 2016). Ag nanorod and cubes were synthesized biologically using sundried *Stevia rebaudiana* leaves (Varshney et al. 2010). Spherical, rod-like, prism, triangular, pentagonal, and hexagonal AgNPs were synthesized by

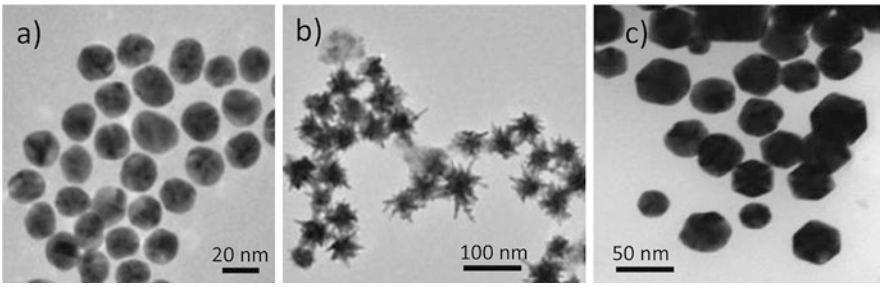

Fig. 2 The TEM image of (**a**) spherical AuNPs and (**b**) star-shaped AuNPs synthesized using *Cistus incanus* extract (Klekotko et al. 2019) and (**c**) spherical/hexagonal AuNPs synthesized using *Acacia nilotica* twig bark extract (Emmanuel et al. 2014)

employing aqueous extract of *Salicornia brachiata* as a bioreducing agent (Seralathan et al. 2014). Spherical and triangular AgNPs in the size range of 6–60 nm were also formed using lingonberry and cranberry juices which contain anthocyanins, benzoic acid, and phenolic compounds (Puišo et al. 2014). Aqueous leaf extract of *Euphorbia prostrata* was resulted in Ag nanorods biofabrication (Zahir and Rahuman 2012). Spherical, triangular, and hexagonal AgNPs were obtained from *Caesalpinia coriaria* leaf extract while its boiling leaf extract yielded only triangular nanoparticles (Jeeva et al. 2014). Cylindrical shaped AgNPs with an average diameter of 250 nm were formed using aqueous bark extract of *Ficus racemosa* (Velayutham et al. 2013). Spherical and triangular AuNPs with the mean diameter of 12–38 nm were yielded using aqueous root extract of *Morinda citrifolia L.* (Suman et al. 2014). Green synthesis of hexagonal AuNPs was carried out utilizing essential oils extracted from fresh leaves of *Anacardium occidentale* (Sheny et al. 2012). It can be seen some TEM images of plant-mediated AuNPs in Fig. 2. Recently, plant-based biosynthesis of metal nanoparticles appeared to be an important branch of green synthesis route which could be an attractive and appropriate alternative to chemical methods and also microorganism-mediated synthetic methods. Hence, some recent studies for the biosynthesis of Ag and AuNPs using plants have been summarized in Table 2.

3 Assisted Green Synthesis of Metal Nanoparticles Using Sunlight, Microwave, and Ultrasound

In an effort to develop environmentally benign green synthesis approaches and reduce energy consumption, alternative assisting energy resources have emerged. The assisting resources are effective for reducing time and temperature of synthesis procedure and yield to create nanoparticles with a higher degree of crystallinity compared to the traditional heating methods (Kahrilas et al. 2013). Sunlight as the

Table 2 Plant-based synthesis of silver and gold nanoparticles

Plant	Metal nanoparticle	Size and shape	Ref.
Camellia sinensis (green tea and black tea leaf extracts)	Ag Au	Au 10 nm Ag 30 nm	Onitsuka et al. (2019)
Amomum villosum (Fructus Amomi (cardamom)) (aqueous extract of dried fruits)	Ag Au	5–10 nm (Au), spherical 5–15 nm (Ag), spherical	Soshnikova et al. (2018)
Aglaia elaeagnoidea (flower extract)	Ag Au	17 nm (Ag), spherical 25 nm (Au), spherical	Manjari et al. (2017)
Camellia sinensis (green tea extract)	Ag	34.68 ± 4.95 nm, spherical	Rolim et al. (2019)
Berberis vulgaris (leaf and root extracts)	Ag	30–70 nm, spherical	Behravan et al. (2019)
Enicostemma axillare (Lam.) (leaf extract)	Ag	15–20 nm, spherical	Raj et al. (2018)
Geranium (*P. hortorum*) (leaf extract)	Ag	25–150 nm	Rivera-Rangel et al. (2018)
Cratoxylum formosum (leaf extract) *Phoebe lanceolata* (leaf extract) *Scurrula parasitica* (aerial parts) *Ceratostigma minus* (stem and root extracts) *Mucuna birdwoodiana* (stem ectract) *Myrsine africana* (root extract) *Lindera strychnifolia* (root extract)	Ag	8.8 ± 0.3 nm ~ 35.4 ± 5.9 nm, spherical	Ahn et al. (2019)
Dodonaea viscosa (leaf extract)	Ag	20–50 nm for nano worms, 50–100 nm for flowers, 70–100 nm for spherical particles and micro sized dendrites (with a diameter about 0.7–2.5 μm and length about 3.3–30 μm)	Anandan et al. (2019)
Rosa brunonii Lindl.	Ag	Less than 100 nm	Bhagat et al. (2019)
Capparis decidua	Ag	1–20 nm, spherical	Ahlawat and Sehrawat (2017)

(continued)

Table 2 (continued)

Plant	Metal nanoparticle	Size and shape	Ref.
Rheum palmatum (root extract)	Ag	44–113 nm, spherical and hexagonal	Arokiyaraj et al. (2017)
Prunus persica L. (outer peel extract)	Ag	28.27 nm, spherical	Patra and Baek (2016)
Cleome viscosa (fruit extract)	Ag	20–50 nm, spherical	Lakshmanan et al. (2018)
Andean blackberry (fruit extract)	Ag	12–50 nm, spherical	Kumar et al. (2017a)
Alpinia Katsumadai (seed extract)	Ag	12.6 nm, quasi-spherical	He et al. (2017)
Nigella arvensis (seed extract)	Ag	2–15 nm, spherical	Chahardoli et al. (2017)
Cucurbita pepo L. (leaf extract)	Au	10–15 nm, spherical	Gonnelli et al. (2018)
Simarouba glauca (leaf extract)	Au	Prism and spherical like particles	Thangamani and Bhuvaneshwari (2019)
Cistus incanus (dried, powdered leaves)	Au	45–85 nm, popcorn-shape	Klekotko et al. (2019)
Sansevieria roxburghiana (leaf extract)	Au	5–31.11 nm (ave 17.48 nm), spherical with a few triangle, hexagonal, rod and decahedral shaped particles	Kumar et al. (2019)
Waste macadamia nut shells	Au	50 nm–2 μm, spherical, triangular and hexagonal morphology	Dang et al. (2019)
Euphrasia officinalis (leaf extract)	Au	5–30 nm, spherical or hexagonal	Liu et al. (2019)
Terminalia arjuna (leaf extract)	Au	15–30 nm, spherical	Dudhane et al. (2019)
Dalbergia coromandeliana (root extract)	Au	10.5 nm, spherical	Umamaheswari et al. (2018)
Waste *Citrullis lanatus var* (watermelon)	Au	100 nm–2.5 μm, spheres and hexagonal plates	Chums-ard et al. (2019)
Gnidia glauca	Au	10–60 nm, spherical	Ghosh et al. (2016)
Pterocarpus santalinus L. (red Sanders) (bark extract)	Au	13–26 nm, spherical	Keshavamurthy et al. (2018)

largest available renewable energy source (Annadhasan et al. 2014; Annadhasan et al. 2015), microwave irradiation (Francis et al. 2018; Shore 2018), and ultrasound radiation (Elsupikhe et al. 2015) as nontoxic, clean, and safe sources have been studied for assisted green synthesis of different kind of nanostructures including plasmonic metal nanoparticles. These alternative sources can assist microorganisms, plant extracts, and active biomolecules to catalyze the formation of nanoparticles.

Microwave-assisted synthesis of metal nanoparticles provides rapid and uniform heating and thus results in homogeneous nucleation and growth condition and consequently narrow size distribution and controlled morphology (Francis et al. 2018; Shore 2018; Kahrilas et al. 2013). Ultrasound-assisted synthesis method is another preferred route for green synthesis of metal nanoparticles based on the application of powerful ultrasound radiation. The ultrasound radiation generates cavitation microbubbles. The bubbles grow in the solution and then collapse after reaching the maximum size. The collapse of bubbles results in extremely high pressure and high temperature. Consequently, this condition causes formation of highly reactive free radicals. It has been reported that using the ultrasound-mediated synthesis method can produce monodispersed nanoparticles with different shapes (Elsupikhe et al. 2015).

4 Application of Green-Synthesized Metal Nanoparticles in Sensing Approaches

Green-synthesized metal nanoparticles have displayed great potential for application in different fields including industry, biotechnology, medicine, food safety, and environmental studies. According to most of the reports, produced metal nanoparticles using green methods exhibit strong antibacterial activity (Koduru et al. 2018) and can be also applied as carriers for drug delivery (Saratale et al. 2018a), biosensor (Gayda et al. 2019), nanocatalyst (Palomo and Filice 2016), and environmental monitoring platform (Saratale et al. 2018b). Due to industrial development and intensive use of toxic chemicals, the level of environmental pollution is increasing. Therefore, there is an environmental concern to monitoring harmful chemicals and removal of contaminations from environmental resources. Moreover, the development of nanotechnology has led to excessive use of chemicals and can also result in a new class of hazardous materials and environmental concern (Masciangioli and Zhang 2003). Therefore, green synthesis for clean production of nanoparticles and monitoring of the potential environmental hazards such as heavy metal ions and organic contaminants have become a vital need to explore the sustainable method for new remedial technologies (Das et al. 2018). To this aim, various novel sensing platforms have been emerged for detection and sensing of toxic chemicals and pollutants by the nontoxic green-synthesized metal nanoparticles. It has been proved that utilizing green-synthesized plasmonic metal nanoparticles as colorimetric

sensors can open up a new window for simple, rapid, and low-cost detection of toxic metal ions and organic compounds in environmental samples (Annadhasan et al. 2014; Ragam and Mathew 2019; Sebastian et al. 2019).

4.1 Colorimetric Detection of Environmental Pollutions

Heavy metals such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), cobalt (Co), nickel (Ni), magnesium (Mn), zinc (Zn), and lead (Pb) have been found highly toxic even in trace level concentrations. So far, several green-synthesized plasmonic metal nanoparticles have shown a promising development in sensing and detection of environmentally toxic heavy metal ions. As mercury ion (Hg^{2+}) and its related compounds are highly toxic, it is of great concern among various toxic heavy metals. Therefore, several sensors have been investigated for the detection of Hg^{2+}. In one work, AgNPs were produced using *Syzygium aromaticum* commonly known as clove. During AgNPs biosynthesis, it was revealed that the size of AgNPs increased by increasing the concentration of Ag ions and temperature. Also, a red-shift was observed in the LSPR absorption band of AgNPs. The biosynthesized AgNPs has been adopted for detection of Hg^{2+} ions in water with a minimum detection level of 2.0 μM. Electrostatic interaction of Hg^{2+} ions with AgNPs led to form Ag–Hg amalgam and consequently caused the color solution to vanish (Sangar et al. 2019). Monodispersed, quasi-spherical AgNPs with an average size of ~11 nm and antibacterial activity were produced using the aqueous extract of an agrowaste: *Terminalia catappa* leaves containing flavonoids, phenolic compounds, and antioxidants which acted as reducing and capping agents. The green-synthesized AgNPs were used as a sensor for the colorimetric detection of trace levels of Hg^{2+} based on the color change of the solution of AgNPs from deep brown to colorless due to redox reaction between Hg^{2+} ions and AgNPs. Moreover, a blue shift and decrease in the LSPR peak intensity were observed in the presence of Hg^{2+} ions (Devadiga et al. 2017). Biologically green-synthesized AgNPs were obtained using a freshly prepared extract of the soap-root plant and aqueous extract of manna of *Hedysarum* plant. The biofabricated yellowish-brown AgNPs were used as a colorimetric sensor for detection Hg^{2+} in water samples with the limit of detection of 2.2 μM. The color of AgNPs solution turned to pale yellow in the presence of Hg^{2+}. Also, the color of the solution decreased gradually with the increase of Hg^{2+} concentration. Finally, it turned to colorless at concentration of 0.001 M of Hg^{2+} ions (Farhadi et al. 2012). Figure 3 shows the changes of the LSPR absorption band and color change of AgNPs solution in the presence of Hg^{2+} and some other heavy metal ions.

Green crystalline AgNPs were synthesized from *Allium sativum* (garlic) extract. The extract of *Allium sativum* is containing amino acids, carbohydrates, and vitamin (vitamin B6). These biomolecules acted as stabilizer. The produced AgNPs were employed as a colorimetric sensor for sensitive detection of Hg^{2+} in the presence of Fe^{3+} in water samples. It was observed that Fe^{3+} was not able to oxidize and etch AgNPs in phosphate buffer. Therefore, the color change from yellow to colorless

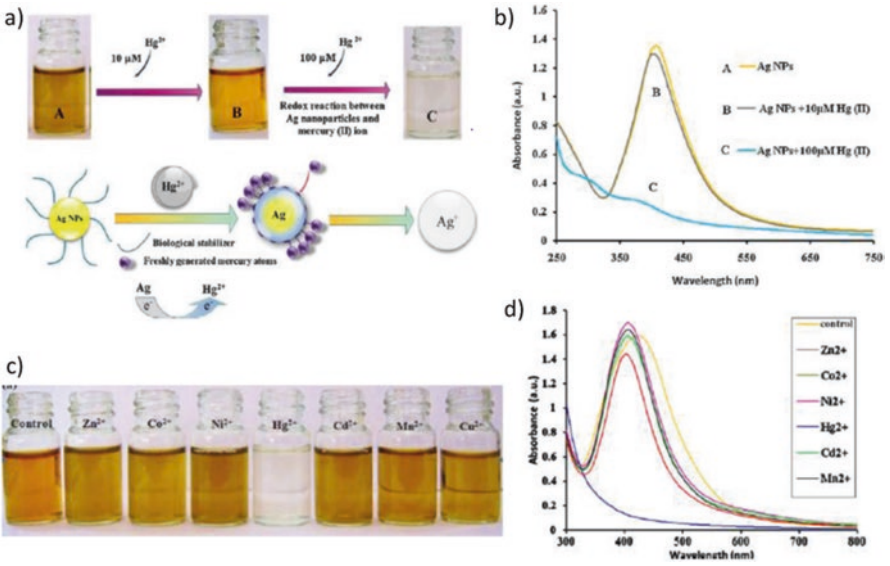

Fig. 3 (**a**) Schematic representation of possible mechanism of Hg^{2+} detection, (**b**) UV-Vis spectra of (*A*) biosynthesized AgNPs, (*B*) AGNPs in after addition of 10 μM of Hg^{2+} and (*C*) 100 μM of Hg^{2+}; (**c**) image of biologically synthesized AgNPs in the presence of Hg^{2+} and other heavy metal ions such as Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, and Cu^{2+} which confirms sensor selectivity; (**d**) UV-Vis spectra of the solution of AgNPs in the presence of the mentioned metal ions (Farhadi et al. 2012)

and the observed blue shift could be due to the interaction of Hg^{2+} and AgNPs. This colorimetric sensor was also useful for colorimetric detection of Pb^{2+} ions in the concentration range of 0.05–1 mM (Ghosh et al. 2018). Biosynthesized AgNPs using an aqueous extract of *Murraya koenigii* were capable of sensitive detection of Hg^{2+} ions based on a redox reaction between Hg^{2+} and AgNPs. Indeed, this sensing probe was evaluated separately for colorimetric detection of various metal ions such as Fe^{3+}, Fe^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Al^{3+}, As^{3+}, As^{5+}, Cu^{2+}, Hg^{2+}, and Mn^{2+}. Only in the presence of Hg^{2+} ions, color change was occurred from dark brown to colorless, the LSPR peak shifted shorter wavelength and its intensity decreased. No color change was observed in the case of other studied metal ions and the intensity of the LSPR absorption band changed slightly (Kumar et al. 2017b). For colorimetric detection of Hg^{2+} in various groundwater samples, a colorimetric sensor was designed based on green-synthesized AgNPs by gum kondagogu. In this study, a highly sensitive colorimetric sensor was proposed for detection of Hg^{2+} in low concentration of 0.05 μM. This enhanced sensitivity could be due to small green-synthesized AgNPs with the average size of 5 ± 2.8 nm (Rastogi et al. 2014). Also, green-synthesized crystalline AgNPs using citrus fruit extracts (lemon, *Citrus limon* and sweet orange, *Citrus limetta*) has been demonstrated as a selective sensing probe for detection of Hg^{2+} ions at wide pH range (3.2–8.5) (Ravi et al. 2013). Synthesized AgNPs using leaf extract of *Dahlia pinnata* showed the ability to selective sensing of hazardous Hg^{2+} ions at wide pH range (3–8) (Roy et al. 2015).

A fully eco-friendly colorimetric assay was proposed for Hg^{2+} detection in drinking water using AgNPs capped with carboxymethyl cellulose which were synthesized by carboxymethylation of cellulose waste isolated from Tunisian pal date petiole. This sensitive sensor exhibited great potential in the successful detection of hazardous Hg^{2+} at a low concentration. The high observed sensitivity can make the proposed sensor as a powerful detection probe applied for water safety control (Sakly et al. 2017). AgNPs with anticancer and catalytic activity generated from aqueous mango leaf extract exhibited selective colorimetric sensing of Hg^{2+} ions in water due to oxidation of AgNPs to Ag^{+} ions and discoloration of solution (Samari et al. 2018). Green-synthesized AgNPs using *Euphorbia geniculate* extract were also evaluated for sensing of Hg^{2+} ions according to the formation of Hg–Ag amalgam and etching of AgNPs (Santhosh et al. 2019). Similarly, green synthesis of AgNPs was achieved using *Panax ginseng* root extract. The produced AgNPs were investigated for colorimetric detection of Hg^{2+} based on fading of the color of AgNP solution due to the dissolution of AgNPs and the formation of Ag–Hg amalgam (Tagad et al. 2017). The synthesized AuNPs by nonpathogenic fungal biomass of *Trichoderma harzianum* were investigated as a colorimetric sensor for Hg^{2+} detection. The sensing strategy was based on aggregation of AuNPs in the presence of Hg^{2+} ions. This interaction led to color change from pink-red to grayish blue. It was also observed that the plasmonic absorption band of AuNPs shifted from 532 to 540 nm through a red shift and a new LSPR peak was appeared at 720 nm. These changes in the color of solution and the LSPR absorption band indicated the Hg^{2+} binding to AuNPs and their aggregation (Tripathi et al. 2014). In another study, a highly selective colorimetric sensor for the detection of Hg^{2+} was reported. Well-dispersed quasi-spherical biofabricated AgNPs using plant extract of *Matricaria recutita* (Babunah) were used for detection of Hg^{2+} ions (Uddin et al. 2017).

Besides the studied nanosensors for detection of Hg^{2+}, several plasmonic sensing platforms have emerged for detection of some other potential toxic heavy metals. Functionalized AuNPs were obtained using *Mangifera indica* leaf extract. The prepared AuNPs were used for colorimetric detection of As^{3+} ions in an aqueous medium with limit of detection of 1.2 ppb. It was observed that As^{3+} ions caused to aggregation of AuNPs and subsequent color change from red to blue. Also, a red shift occurred in the LSPR peak and a new absorption band was appeared ad 525 and 720 nm. These changes indicated aggregation of AuNPs in the presence of As^{3+} ions (Boruah et al. 2019). In another study, AgNPs and AuNPs were prepared using L-tyrosine as reducing and stabilizing agent under ambient sunlight irradiation in aqueous medium and were used as a sensitive plasmonic nanoprobe for detection of metal ions. It was found that green-synthesized AgNPs were sensitive to Hg^{2+} and Mn^{2+} ions. The obtained AuNPs were used for highly sensitive naked-eye detection of Hg^{2+} and Pb^{2+} in drinking water and tap water samples with the detection limit in nM concentrations. Different strategies were reported for detection of Hg^{2+}, Mn^{2+}, and Pb^{2+} ions. A blue shift was observed in the LSPR plasmonic absorption band of AgNPs in the presence of Hg^{2+} ions and the yellow color of the solution turned to colorless. Moreover, the interaction of Hg^{2+} ions with AuNPs led to a blue shift in the LSPR spectrum and the color of the solution remained pink. These observations

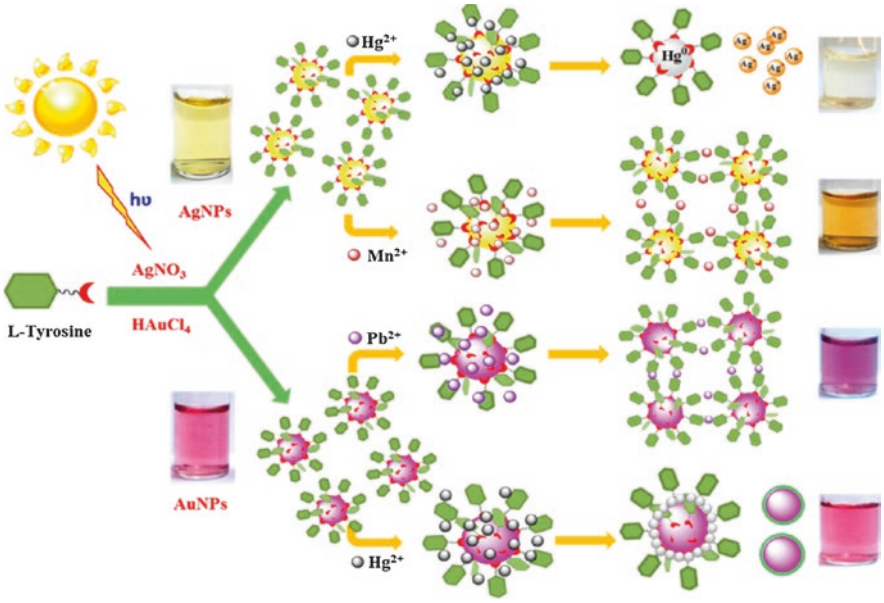

Fig. 4 Colorimetric detection of Hg^{2+} and Mn^{2+} ions using green-synthesized AgNPs and Hg^{2+} and Pb^{2+} ions based on green-synthesized AuNPs (Annadhasan et al. 2014)

confirmed the formation of a core shell structure. Also, aggregation of nanoparticles occurred due to complex formation between Mn^{2+} and Pb^{2+} with L-tyrosine present on the surface of Ag and AuNPs, respectively. As it is known, these aggregations resulted in red shift in the LSPR spectra of nanoparticles (Fig. 4) (Annadhasan et al. 2014).

In a similar report, AuNPs were synthesized using N-cholyl-L-valine under natural sunlight irradiation. The green-synthesized AuNPs were used for colorimetric detection of Co^{2+} and Ni^{2+} in tap water and drinking water. A red shift from 525 nm towards 543 nm was observed in the LSPR absorption band of AuNPs after addition of Ni^{2+} ions to AuNPs solution. This change could be due to Ni^{2+} ion interaction with the functional groups present on the surface of AuNPs. The existing functional groups led to the aggregation of AuNPs. The pink color of the solution turned to purple at lower concentrations of Ni^{2+} and then changed to violet at higher Ni^{2+} concentrations. Also, the color of AuNPs solution turned to pale pink after addition of Co^{2+} ions due to the formation of precipitation of particles (Annadhasan et al. 2015). The biologically synthesized AgNPs were prepared from the leaf extract of *Amomum subulatum* and were used as a selective colorimetric sensor for detection of Zn^{2+} in drinking water. In the sensing process of Zn^{2+} ions, the yellowish-brown color of biosynthesized plasmonic AgNPs changed to colorless and the LSPR absorption band at 425 nm was decreased and slightly shifted to a higher wavelength. This peak was completely disappeared at high concentration of Zn^{2+} (Ihsan et al. 2015). Fresh extracts of different parts of neem were used for green synthesis

of AgNPs. The obtained AgNPs were employed as colorimetric sensors for detection of heavy metal ions. The synthesized AgNPs using fresh neem leaf extracts were used for selective colorimetric detection of Hg^{2+} and fabricated AgNPs via sun-dried neem leaf extract exhibited selective detection of Hg^{2+} and Pb^{2+}. The obtained AgNPs using neem bark extract detected Hg^{2+} and Zn^{2+}. Similarly, synthesized AgNPs using fresh and sun-dried mango leaf and green tea extracts successfully demonstrated selective colorimetric detection of Hg^{2+} and Pb^{2+}. Prepared AgNPs using pepper seed extracts also showed selective colorimetric detection towards Hg^{2+}, Pb^{2+}, and Zn^{2+} (Karthiga and Anthony 2013). A colorimetric sensor was designed for selective naked-eye detection of Pb^{2+} using AgNPs synthesized from leaf extract of *Aconitum violaceum*. The phytosynthesized AgNPs exhibited a color change from yellow to red in the presence of Pb^{2+} ions. The color change was observed due to the interaction of metal ions with catechins found on the surface of AgNPs. The interaction of catechin and Pb^{2+} ions led to aggregation of nanoparticles. Moreover, the LSPR spectrum of AgNPs change after addition of Pb^{2+} ions. A new absorption band was appeared at 520 nm and the intensity of the plasmonic band at 404 nm was decreased (Khan et al. 2018b). The prepared AuNPs using the aqueous leaf extract of *Rosa indica – wichuraiana* hybrid *Francois Guillot* were functionalized with glutathione (GSH). The synthesized GSH-AuNPs were employed as a highly responsive sensor for colorimetric detection of Cd^{2+}. The proposed sensor showed color change from ruby red to purple due to the aggregation of GSH-AuNPs in the presence of Cd^{2+} (Manjumeena et al. 2015). AuNPs were prepared using the extracellular culture filtrate of the fungus *Aspergillus candidus* IF1. The biogenic AuNPs exhibited rapid aggregation by addition of cerium (Ce) and were demonstrated as a fast, precise colorimetric sensor towards Ce^{3+}. It was revealed that the aggregation was due to the formation of a coordinate complex between Ce^{3+} ions and –COOH and –NH functional groups present on the surface of AuNPs. The interaction between Ce^{3+} ions and AuNPs led to color change from red to purple (Priyadarshini et al. 2015). Riboflavin-functionalized AgNPs were synthesized using the *Cucumis melo* juice via a green synthesis approach. The prepared AgNPs were used as a colorimetric sensing platform for the selective and sensitive detection of trace concentrations of Cu^{2+} ions in ground and tap water. In this study, colorimetric detection of Cu^{2+} ions was performed based on the accelerated etching of AgNPs which resulted in the fading of yellow color of AgNPs and decrease of the LSPR absorption band intensity (Basiri et al. 2017). In another study, AgNPs were obtained using an aqueous extract of *Ficus benjamina* leaves and were evaluated as a colorimetric sensor for Zn^{2+} detection. Upon addition of Zn^{2+} ion to AgNPs solution, the yellow color of the solution turned to orange due to the aggregation of nanoparticles (Puente et al. 2019). The synthesized AgNPs using *Acalypha hispida* leaf extract showed a colorimetric response to detect a very low concentration of Mn^{2+} in industrial effluent. Aggregation of AgNPs was observed to due to chelation of Mn^{2+} ions in the presence of capping agents of AgNPs and subsequently a change in color of the solution, from reddish brown color to colorless (Sithara et al. 2017). Some reported green-synthesized plasmonic metal nanoparticles as colorimetric sensors for detection of heavy metal ions and the related analytical parameters are summarized in Table 3.

Table 3 Reported green-synthesized plasmonic nanoparticles as colorimetric sensors for detection of heavy metal ions

Microorganism	Biomolecule	Metal nanoparticle	Size and shape	Metal ion	Linear range	Detection limit	Sample	Ref.
Syzygium aromaticum	Phenolic compounds	Ag	5–10 nm	Hg^{2+}	–	2 μM	–	Sangar et al. (2019)
Terminalia catappa (leaf extract)	Phenolic compounds Flavonoid Antioxidants	Ag	10.9 nm	Hg^{2+}	–	0.85 μg mL^{-1}	–	Devadiga et al. (2017)
Soap-root plant and *Hedysarum*	–	Ag	–	Hg^{2+}	10–100 μM	2.2 μM	Lake water	Farhadi et al. (2012)
Allium sativum (garlic extract)	Amino acids Carbohydrate Vitamin (vitamin B6)	Ag	10 nm, spherical	Hg^{2+} Pb^{2+}	2–200 μM 0.05–1 mM	2 μM	–	Ghosh et al. (2018)
Murraya koenigii (leaf extract)	Tannin Flavonoids	Ag	8.6 nm, spherical	Hg^{2+}	50 nM–500 μM	–	–	Kumar et al. (2017b)
Gum kondagogu	–	Ag	5 ± 2.8 nm,	Hg^{2+}	0.05–1 μM	0.05 μM	Ground water	Rastogi et al. (2014)
Citrus limon *Citrus limetta* (fruit juice)	Citric acid Ascorbic acid	Ag	25–35 nm	Hg^{2+}	–	100 μM Visual detection	Tap water	Ravi et al. (2013)
Dahlia pinnata (leaf extract)	Phenolic compounds Carbohydrates	Ag	15 nm, spherical	Hg^{2+}	–	10 μM Visual detection	–	Roy et al. (2015)
Tunisian date palm petioles	Carboxymethyl cellulose	Ag	–	Hg^{2+}	25–200 nM	5 nM	Drinking water	Sakly et al. (2017)

(continued)

Table 3 (continued)

Microorganism	Biomolecule	Metal nanoparticle	Size and shape	Metal ion	Linear range	Detection limit	Sample	Ref.
Mangifera indica Mango (leaf extract)	Phenolic compound Flavonoid	Ag	20.7 nm, spherical	Hg^{2+}	1–517 µM	–	–	Samari et al. (2018)
Euphorbia geniculata (leaf extract)	Alkaloids Flavonoids Polyphenols	Ag	17 nm	Hg^{2+}	10–120 ppm	10 ppm	–	Santhosh et al. (2019)
Panax ginseng (root extract)	–	Ag	4–20 nm, spherical	Hg^{2+}	10 µM–1 mM	5 µM	–	Tagad et al. (2017)
Trichoderma harzianum (Fungi)	Protein Cysteine Enzyme	Au	26–34 nm, spherical	Hg^{2+}	0.001–1 µM	2.6 nM	Tap water Ground water	Tripathi et al. (2014)
Matricaria recutita (stem extract)	Terpenoids Flavonoids Coumarins Polysaccharides	Ag	11 nm, overall quasi-spherical	Hg^{2+}	5–15 ppm	5 ppm	–	Uddin et al. (2017)
Mangifera indica (leaf extract)	Flavonoids Terpenoids Thiamine	Au	Spherical	As^{3+}	1–11 ppb	1.2 ppb	–	Boruah et al. (2019)

–	L-tyrosine	Ag	8.2–32 nm, spherical, ellipsoids and rods	Hg^{2+} Mn^{2+}	Hg^{2+}: 20–150 nM Mn^{2+}: 20–200 nM	Hg^{2+}: 19 nM (drinking water) and 26 nM (tap water) Mn^{2+}: 23 nM (drinking water) and 26 nM (tap water)	Drinking water Tap water	Annadhasan et al. (2014)
		Au	17–36 nm, spherical	Hg^{2+} Pb^{2+}	Hg^{2+}: 60–200 nM Pb^{2+}: 20–100 nM	Hg^{2+}: 60 nM (drinking water) and 72 nM (tap water) Pb^{2+}: 23 nM (drinking water) and 26 nM (tap water)		
–	*N*-cholyl-L-valine (NaValC)	Au	8–40 nm, spherical	Co^{2+} Ni^{2+}	5–40 nM	10 nM	Drinking water Tap water	Annadhasan et al. (2015)
Amomum subulatum (leaf extract)	Phenolic compounds	Ag	20–50 nm, spherical	Zn^{2+}	10–80 μM	3.5 μM	Drinking water	Ihsan et al. (2015)
Neem (leaf and bark extract) Mango (leaf extract) Green tea Paper (seed extract)	Gallic acid Catechin Phenolic compounds Flavonoids	Ag	Spherical	Hg^{2+} Pb^{2+} Zn^{2+}	–	–	–	Karthiga and Anthony (2013)

(continued)

Table 3 (continued)

Microorganism	Biomolecule	Metal nanoparticle	Size and shape	Metal ion	Linear range	Detection limit	Sample	Ref.
Aconitum violaceum (leaf extract)	Polyphenols (catechin)	Ag	20 nm, spherical	Pb^{2+}	0.5–25 μM	0.1 μM	River water	Khan et al. (2018b)
Rosa indica-wichuriana hybrid Francois guillot (leaf extract)	–	Au	5–13 nm, spherical	Cd^{2+}	–	30 nM 70 nM	Water sample	Manjumeena et al. (2015)
Aspergillus candidus IF1 (Fungi extract)	Protein Peptide Carbohydrate	Au	22–25 nm, spherical	Ce^{3+}	2–50 ppm	15 ppm (DLS) 35 ppm (UV–Vis)	–	Priyadarshini et al. (2015)
Cucumis melo (juice)	Vitamin A Vitamin C Riboflavin	Ag	20 nm	Cu^{2+}	5–100 nM	1.12 nM	Ground water Tap water	Basiri et al. (2017)
Ficus benjamina (leaf extract)	–	Ag	11.5 nm, spherical	Zn^{2+}	0.2–2 mM	0.2 mM	–	Puente et al. (2019)
Acalypha hispida (leaf extract)	Phenolic compounds	Ag	20–50 nm	Mn^{2+}	50–250 μM	50 μM	Industrial effluent	Sithara et al. (2017)
Momordica charantia (fruit extract from peel, seed, and seed coat)	Phenolic compounds	Au	–	Cd^{2+}	0.2–0.8 ppm (0.18–0.71 μM)	0.186 μM	–	Singh et al. (2018a)

The biologically obtained plasmonic nanoparticles were also evaluated for detection of other types of pollutants. In-situ green fabrication of AgNPs was reported using flexible and transparent bacterial cellulose nanopapers. In this biosynthesis method, first Ag ions were adsorbed on bacterial cellulose nanopaper and then were reduced to AgNPs by the hydroxyl groups of cellulose nanofibers. The resulted AgNPs were employed as a sensitive sensing probe for the detection of cyanide ion (CN^-) and 2-mercaptobenzothiazole in water samples (Pourreza et al. 2015). Epigallocatechin gallate isolated from green tea synthesized AgNPs. A sensitive colorimetric sensor was established using the as-prepared stable AgNPs for colorimetric detection of kanamycin and sulfide ions (Singh et al. 2018b). Stable AuNPs were obtained using *Momordica charantia* fruit extract (peel, seed, and seed coat) and were evaluated as a colorimetric sensor for detection of Cd^{2+} and thiophenol. The mechanism of colorimetric detection for both analytes was based on the aggregation of AuNPs and color of AuNPs solution changed from red to violet (Singh et al. 2018a).

In several studies, the application of nontoxic and eco-friendly metal nanoparticles as a dual or multifunctional sensor has been demonstrated. Moreover, these green prepared metal nanoparticles have been employed in other sensing approaches like electrochemical, fluorescence, or surface enhanced Raman spectroscopy (SERS). The obtained AgNPs from *Agaricus bisporus* were used for optical and electrochemical sensing of Hg^{2+} ions (Sebastian et al. 2018). A biogenic route was developed for the synthesis of AuNPs with tunable size using *Citrus paradisi* extract. It was observed that the biofabricated AuNPs were able to detect Pb^{2+}, Cu^{2+}, Hg^{2+}, Zn^{2+}, and Ca^{2+} ions through both fluorescent and plasmonic sensing strategies (Silva-De Hoyos et al. 2020). A multifunctional sensing approach was investigated for detection of Cu^{2+} ions via biosynthesized AgNPs. The AgNPs have been obtained using bark extract of *Moringa oleifera*. These AgNPs were employed as a sensing probe for colorimetric, fluorescence, and electrochemical sensing of Cu^{2+} ions (Sebastian et al. 2019). A dual sensor was developed for the detection of Thiram (toxic dithiocarbamate fungicide) using both colorimetric and electrochemical sensing methods. The crystalline spherical AgNPs which have been synthesized biologically by the stem extract of *Coscinium fenestratum* were exploited as a sensing probe for detection of Thiram in tap, canal, and river water samples (Ragam and Mathew 2019). Eco-friendly stable monometallic Ag and AuNPs and also bimetallic Ag/Au alloy nanoparticles were fabricated using Indian curry leaf plant (*Murraya koenigii Spreng*) under sonochemical condition at room temperature and pressure. These nanoparticles were employed for fluorometric detection of hazardous dithiocarbamate pesticide like Mancozbe in an aqueous medium (Alam et al. 2016). AuNPs were synthesized using *Acacia Nilotica* twig bark extract at room temperature and was employed for trace level electrochemical detection of nitrobenzene which is known as a hazardous pollutant (Emmanuel et al. 2014).

4.2 SERS-Based Green Sensors for Detection of Environmental Pollutions

SERS as an advanced powerful analytical technique enables simple and rapid detection of various analytes in a single molecular level. In some reported studies, green-synthesized silver or gold nanoparticles were considered as SERS substrates for detection of numerous environmental pollutions. In one work, prepared Au–Ag core–shell and alloy nanoparticles using xylan extracted from bagasse were evaluated as a probe for detection of a common food contaminant, Sudan I. Xylan-capped Au@Ag nanoparticles with the advantage of enhanced Raman performance were able to detect trace concentration of Sudan I with detection limit of 0.126 ppm (Cai et al. 2019). Green-synthesized silver nanoparticle-reduced graphene oxide nanocomposite using *Psidium guajava* exhibited remarkable surface enhanced Raman signal for detection of methylene blue with a limit of detection of 0.01 μM (Chettri et al. 2017). In-situ synthesized AuNPs using a common edible fungus, *Tremella fuciformis* (TF) were used as a SERS substrate for trace detection of cationic dyes like methylene blue, Congo red and crystal violet as water contaminations. The TF as a capping agent on AuNPs prevented the aggregation of nanoparticles. It also provided an effective surface for adsorption of dyes which caused significant Raman signal enhancement (Tang et al. 2018). Bimetallic Au@Ag nanostructures were obtained through green synthesis using epigallocatechin Gallate isolated from tea leaves. These green-synthesized nanoparticles exhibited strong SERS signal for detection of Rhodamine 6G (Wang et al. 2016b). In another study, biosynthesized AuNPs using IPE of bacterial strain *Staphylococcus warneri* exhibited enhanced SERS signal towards detection of Rhodamine 6G. According to the obtained results, it was revealed that the green-synthesized AuNPs could be a superior SERS substrate for sensitive detection of different toxic chemical compounds, organic pollutants like nitro aromatics and dyes at a single molecular level (Nag et al. 2018).

5 Conclusion

This chapter focuses on the green and biological synthesis of metal nanoparticles and their application in sensing and detection of heavy metal ions and organic pollutants. Green synthesis of metal nanoparticles has displayed several advantages over traditional chemical methods such as producing environmental friendly and biocompatible nanoparticles, preventing the use of chemical reagents, and decreasing the formation of hazardous by-products and their side effects. Therefore, green synthesis method has been evolved as an important and popular synthetic branch of nanotechnology due to its advantages. Different microorganisms like bacteria, yeasts, fungi, and algae, and plants and pure bioagents have been described as potential biological nanofactories for the generation of metal nanoparticles. The green-synthesized nanoparticles are successfully being used in numerous

applications including biological and food analysis, drug delivery, environmental monitoring, and sensing approaches. By increasing the level of harmful pollutants, there is an environmental concern to sensing and removal of toxic compounds. By considering unique properties of plasmonic metal nanoparticles, different LSPR-based sensors have been designed employing biosynthesized metal nanoparticles for detection of several toxic heavy metal ions and organic pollutants. Colorimetric and SERS-based sensors as powerful and highly selective and sensitive detection methods using nontoxic nanoparticles can provide a promising opportunity for simple and rapid detection of pollutants in soil and water resources, as attractive sensing methods for environmental monitoring applications.

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