Chapter 17
Gold Nanoparticles from Plant System: Synthesis, Characterization and their Application

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17.1 Introduction

Nanotechnology is science, engineering and technology conducted at the nanoscale (at least one dimension between 1 and 100 nm). The unique physicochemical feature of these nanomaterials is not observed in the corresponding bulk materials (Nel et al. 2006). Hence, they have gained huge attention in industry and technology. Over the past few years, synthesis of nanomaterials and their characterization has accelerated due to huge applications in various fields of biology, chemistry, physics and medicine. The main concerns with chemical synthetic routes are environmental contamination, and physical methods need enormous amount of energy to maintain the high pressure and temperature. Moreover, chemical and physical methods are usually expensive processes. Many researchers have diverted their interest to biological synthesis of nanoparticles. Plants and plant-related product synthesis of nanomaterials are generally simple, inexpensive, available and eco-friendly (Husen and Siddiqi 2014a, b, c; Yasmin et al. 2014; Pasca et al. 2014; Prasad 2014; Khan et al. 2015; Yu et al. 2016; Tripathi et al. 2016; Siddiqi and Husen 2016a). It is understood that in comparison to microorganism-mediated synthesis of nanoparticles, the use of plants and plant-related products is more advantageous due to the ease of scaling up, less biohazards on production and elimination of the elaborate process of maintaining cell cultures. Thus, exploring plants with high metal accumulation capacity/phytomining, as well as its engineering, is a need of the hour (Husen and Siddiqi 2014b; Iqbal et al. 2015).

Plants or their extracts/products have been extensively used to produce a range of metal nanoparticles with well-defined size and shape (Husen and Siddiqi 2014b).

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Gold acquires elite properties, namely, high free electron density, malleability and conductivity, and favours opportunities to produce stable and adjustable gold nanoparticles for potential applications, for instance, in diagnostics, biological imaging, biosensors, therapeutic agent delivery, photodynamic therapy, electronics, catalytic activity, antioxidant, antibacterial, larvicidal activity, environmental monitoring/cleanup, etc. (Castaneda et al. 2007; Chen et al. 2008; Baruah and Dutta 2009; Yeh et al. 2012; Spivak et al. 2013; Kesik et al. 2013; Kumar et al. 2013; Husen and Siddiqi 2014b; Li et al. 2014; Kuppusamy et al. 2015; Yu et al. 2016).

It is well known that in the biological process, extracts from the living system served as reducing and capping agents. Numerous routes have been developed for the biological or biogenic synthesis of gold nanoparticles from the corresponding salts. In this connection, plants have been proven to be capable for the rapid intra- or extracellular synthesis of gold nanoparticles such as *Acacia nilotica* (Majumdar et al. 2013), *Achyranthes aspera* (Tripathi et al. 2016), *Azadirachta indica* (Ramezani et al. 2008), *Beta vulgaris* (97), *Brassica juncea* (Arora et al. 2012), *Camellia sinensis* (Vilchis-Nestor et al. 2008), *Cicer arietinum* (Ghule et al. 2006), *Cinnamomum camphora* (Huang et al. 2007), *Citrus maxima* (Yu et al. 2016), *Cymbopogon flexuosus* (Shankar et al. 2004a), *Euphorbia hirta* (Annamalai et al. 2013), *Hamamelis virginiana* (Pasca et al. 2014), *Madhuca longifolia* (Fayaz et al. 2011), *Salicornia brachiata* (Ahmed et al. 2014), *Vitis vinifera* (Ismail et al. 2014), *Zingiber officinale* (Kumar et al. 2011) and so on (Fig. 17.1 and Table 17.1). Hence based on this information, the present review was focused on the plant-mediated syntheses of gold nanoparticles, possible mechanisms, characterization as well as the potential applications in various fields, including medicine, industry, agriculture and pharmaceuticals.

17.2 Phytosynthesis of Gold Nanoparticles

Phytosynthesis of gold nanoparticles depends on several important factors such as concentration of plant extract or biomass, concentration of metal salt, incubation/reaction time, temperature and pH of the solution (Fig. 17.2). Thus, by establishing the relationship of these factors with size and shape of the concerned nanoparticles, it is possible to obtain nanoparticles of the desired properties in a controlled way. Plant extract or biomass can be prepared from various parts of plant (leaves, stems, roots, shoots, barks, seeds, flowers or floral parts) or the whole plant. Usually, for the extraction procedure, the desired plant parts are soaked in a solvent. The obtained plant extract contained the reducing and capping agents needed to reduce metallic ions. The advantage of using dried desired plant parts is that these can be stored at room temperature for a longer period of time if at all required, while to prevent deterioration, the fresh plant/plant parts should be stored at −20 °C. In addition, the variation due to seasonal fluctuations which lead to the variations in plant constituents is eliminated by using dried materials (Huang et al. 2007; Sheny et al. 2011). It is well known that plants or their extracts contain different

Fig. 17.1 Plants and their parts used for fabrication of gold nanoparticles

biomolecules such as proteins, sugars, amino acids, enzymes and other traces of metals. These metabolites are strongly involved in the bioreduction process.

The main idea behind the nanoparticle formation is the reduction of metal ion to elemental metal. It has been reported that due to the limited capacity of plants for reducing metal ions, the biosynthetic process usually works well for metal ions with large positive electrochemical potential such as Au and Ag ions (Haverkamp and Marshall 2009). Synthesis of gold nanoparticles was carried out by Shankar et al. (2003) using geranium (*Pelargonium graveolens*) leaf extract. The shape of the gold nanoparticles was spherical, triangular, decahedral and icosahedral. This reaction was completed within 48 h. Authors proposed that the terpenoids in the leaf extract may be responsible for the reduction of gold ions and formation of gold nanoparticles. Synthesis of gold nanoparticles using Fourier transform infrared (FTIR) spectroscopy exhibited that the flavanones and terpenoids which are abundant in *Azadirachta indica* leaf broth have probably been adsorbed on the surface of the nanoparticles and led to their stability for 4 weeks (Shankar et al. 2004b). In this

Table 17.1 Phytosynthesis of gold nanoparticles with their size and shape

Plant	Part used	Size	Shape	References
Acacia nilotica	Leaves	6–12 nm	Spherical	Majumdar et al. (2013)
Aegle marmelos	Leaves	38.2 ± 10.5 nm	Spherical	Rao and Paria (2014)
Aerva lanata	Leaves	17.97 nm	–	Joseph and Mathew (2015)
Aloe vera	Leaves	–	Crystalline	Chandran et al. (2006)
Angelica archangelica	Root	3–4 nm	Spherical, ovals, polyhedral	Pasca et al. (2014)
Azadirachta indica	Leaves	5.5−7.5 nm	Crystalline	Ramezani et al. (2008)
Beta vulgaris	Sugar beet pulp		Spherical, rod-shaped nanowires	Castro et al. (2011)
Brassica juncea	Leaves	10−20 nm	Near spherical	Arora et al. (2012)
Cacumen platycladi	Leaves	2.2−42.8 nm	Face-centred cubic (fcc) crystalline	Zhan et al. (2011)
Camellia sinensis	Leaves (tea bag)	40 nm	Spherical, triangular, irregular	Vilchis-Nestor et al. (2008)
Chenopodium album	Leaves	10–30 nm	Quasi-spherical	Dwivedi and Gopal (2010)
Cicer arietinum	Bean	–	Triangular	Ghule et al. (2006)
Cinnamomum camphora	Leaves	80, 23.4, 21.5 nm	Spherical, triangular	Huang et al. (2007)
Cinnamomum zeylanicum	Leaves	25 nm	Spherical, prism	Smitha et al. (2009)
Coleus amboinicus	Leaves	4.6–55.1 nm	Spherical, triangular, truncated triangular, hexagonal, decahedral	Narayanan and Sakthivel (2010)
Coriandrum sativum	Leaves	6.7−57.9 nm	Spherical, triangular, truncated, triangular, decahedral	Narayanan and Sakthivel (2008)
Cuminum cyminum	Seed	1−10 nm	Spherical	Krishnamurthy et al. (2011)
Cymbopogon flexuosus	Leaf	12–30 nm	Triangular	Shankar et al. (2004a)
Diopyros kaki	Leaves	5−300 nm	Spherical, triangular, pentagonal, hexagonal	Song et al. (2009)
Emblica officinalis	Fruit	15−25 nm	–	Ankamwar et al. (2005a)

(continued)

Table 17.1 (continued)

Plant	Part used	Size	Shape	References
Eucalyptus camaldulensis	Leaves	5.5−7.5 nm	Crystalline	Ramezani et al. (2008)
Euphorbia hirta	Leaves	6–71 nm	Spherical	Annamalai et al. (2013)
Hypericum perforatum	Bark	4–6 nm	Spherical, polyhedral	Pasca et al. (2014)
Hamamelis virginiana	Bark	4–6 nm	Spherical, polyhedral	Pasca et al. (2014)
Madhuca longifolia	Leaves	–	Triangular, spherical, hexagonal nanoplates	Fayaz et al. (2011)
Magnolia kobus	Leaves	5−300 nm	Spherical, triangular, pentagonal, hexagonal	Song et al. (2009)
Mangifera indica	Leaves	17−20 nm	Spherical	Phillip (2010)
Memecylon edule	Leaves	10−45 nm	Circular, triangular, hexagonal	Elavazhagan et al. (2011)
Menta piperita	Leaves	150 nm	Spherical	Ali et al. (2011)
Momordica charantia	Fruit	500–600 nm	–	Pandey et al. (2012)
Morinda citrifolia	Root	12.17–38.26 nm	Cubic	Suman et al. (2014)
Murraya koenigii	Leaves	20 nm	Spherical, triangular	Philip et al. (2011)
Nyctanthes arbor-tristis	Flower	19.8 nm	Spherical, triangular, hexagonal	Das et al. (2011)
Pelargonium graveolens	Leaves	20−40 nm	Decahedral, icosahedral	Shankar et al. (2003)
Pelargonium roseum	Leaves	5.5−7.5 nm	Crystalline	Ramezani et al. (2008)
Pistacia integerrima	Gall	20–200 nm	–	Islam et al. (2015a)
Psidium guajava	Leaves	25−30 nm	Spherical	Raghunandan et al. (2009)
Punica granatum	Juice	23–36 nm	Triangular, pentagonal, hexagonal, spherical	Dash and Bag (2014)
Rosa hybrida	Petal	~10 nm	Spherical, triangular, hexagonal	Noruzi et al. (2011)
Rosa rugosa	Leaves	11 nm	Triangular and hexagonal	Dubey et al. (2010a)
Salix alba	Leaves	50–80 nm	–	Islam et al. (2015b)
Sesbania drummondii	Seed	6–20 nm	Spherical	Sharma et al. (2007)
Sphaeranthus amaranthoides	Leaves	39 nm	Spherical	Nellore et al. (2012)

(continued)

Table 17.1 (continued)

Plant	Part used	Size	Shape	References
Stevia rebaudiana	Leaves	8−20 nm	Octahedral	Mishra et al. (2010)
Salicornia brachiata	Plant	22–35 nm	Spherical	Ahmed et al. (2014)
Tanacetum vulgare	Fruit	11 nm	Triangular	Dubey et al. (2010b)
Terminalia catappa	Leaves	10−35 nm	Spherical	Ankamwar (2010)
Terminalia arjuna	Fruit	20–50 nm	Spherical	Gopinath et al. (2014)
Terminalia arjuna	Bark	15–20 nm	Triangular, tetragonal, pentagonal, hexagonal, rod-like, spherical	Majumdar and Bag (2012)
Trigonella foenum-graecum	Seeds	15−25 nm	Spherical	Aromal and Philip (2012)
Vitis vinifera	Leaves	18–25	Triangular, pentagonal, spherical	Ismail et al. (2014)
Zingiber officinale	Roots	5–15 nm	Spherical	Kumar et al. (2011)

study, the morphology of the gold nanoparticles was predominantly planar (triangular and a few hexagonal) along with spherical shapes. Control over shape and size of gold nanoparticles has been achieved using *Cymbopogon flexuosus* extract. Anisotropic gold nanotriangles have been synthesized by the reaction of lemongrass extract with aqueous gold ions. In this study, 45 % of the population of total gold nanoparticles was triangular in shape in the range of 0.05–1.8 μm, while other shapes were spherical, hexagonal and cubic. Triangle size was controlled by varying the concentration of the lemongrass extract in the reaction medium. Authors have claimed that with increasing amounts of extract added to the $HAuCl_4$ solution, the average size of the triangular and hexagonal particles decreased, while the ratio of the number of spherical nanoparticles to triangular/hexagonal particles increased (Shankar et al. 2004a). Transmission electron microscopy (TEM) analysis revealed that the most polar fraction produces only triangular shapes similar to that produced by the total extract, while the most non-polar fraction produces only cubic shapes. The study of the FTIR and nuclear magnetic resonance (NMR) spectroscopy of the most polar reaction exhibited that aldehydes and ketones were responsible for the stabilization and formation of gold nanoparticles. These gold nanotriangles might be building blocks for the synthesis of electrically conductive thin films (coatings), which can be used effectively in vapour sensing. Bioreduction of $HAuCl_4$ using tamarind leaf extract led to the formation of flat and thin single crystalline gold nanotriangles with unique and highly anisotropic planar shapes. These gold nanotriangles may find application in

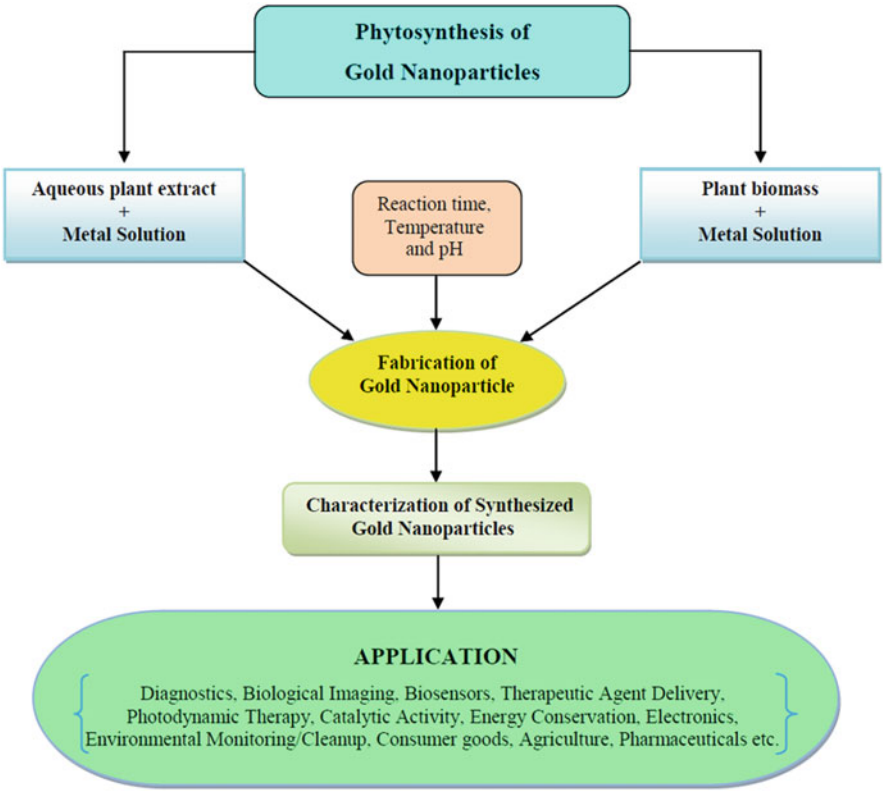

Fig. 17.2 Phytosynthesis of gold nanoparticles from aqueous plant extract/biomass and their application

photonics, optoelectronics and optical sensing (Ankamwar et al. 2005b). Proteins and other biomolecules from *Cicer arietinum* mediate the bioreduction of aqueous Au (III) ions directing the formation of microscale triangular gold prisms (Ghule et al. 2006). Control of the morphology of gold nanoparticles has been achieved by varying compositions of *C. arietinum* extract and aqueous Au (III) solution.

The shape and size of the synthesized gold nanoparticles were modulated and produced by *Aloe vera* leaf extract (Chandran et al. 2006). The gold nanoparticles were triangular and ranged from 50 to 350 nm, which was dependent on the quantity of leaf extract. When a low amount of leaf extract was added to $HAuCl_4$ solution, the fabrications of nanogold triangles were larger in sizes. Moreover, when the quantity of leaf extract was increased, the ratio of nanogold triangles to spherical was decreased. In this study, carbonyl functional groups were found to be responsible for the reduction of gold ions and production of nanoparticles. As progress is made in green synthesis, instead of using the plant extract by boiling, the sun-dried leaf powder in water at ambient temperature is used in some studies. In this type of nanoparticle fabrication, a moderator and accelerator like ammonia

was not needed, but the leaf extract concentration was the rate-determining step. It was an important move in bioreduction of $AuCl_4^-$ that biomolecules of molecular weight less than 3 kDa can cause its reduction. *Cinnamomum camphora* sun-dried powder of leaves was used for the production of gold and silver nanoparticles (Huang et al. 2007). *Mangifera indica* leaf (extract and dried powder) was also used to produce spherical gold nanoparticles at room temperature (Philip 2010). The author claimed that the smaller and more uniform size of gold nanoparticles can be produced by dried *M. indica* leaves. The size of the gold nanoparticles was larger in lower extract quantities perhaps due to lack of stabilizing biomolecules in small quantities. These gold nanoparticles were stable for more than 5 months. The FTIR study exhibited the role of water-soluble compounds, for instance, flavonoids, terpenoids and thiamine as stabilizing agents in the synthesis of gold nanoparticles.

Phyllanthin an important ingredient of the plant was separated from the extract of *Phyllanthus amarus* by liquid–liquid extraction and chromatography. Thereafter, a purified component was used to synthesize gold nanoparticles. Further, cyclic voltammetry and thermogravimetry were used to verify the conversion of gold ions to zero-valent nanoparticles (Kasthuri et al. 2009). Although pure nanoparticles were obtained, this procedure was more complicated than the traditional plant-mediated methods. Rapid gold nanoparticle synthesis within a short duration has also been shown using marine alga, *Sargassum wightii* (Singaravelu et al. 2007), in which the powder of marine alga with gold ions exhibits the colour change of the medium to ruby red after 15 h of incubation. The algal biomass kinetics was observed between 300 and 800 nm using UV–Vis spectroscopy. The bands corresponding to the surface plasmon resonance (SPR) were found at 527 nm during this gold ion reduction process. Gold nanoparticles were fabricated by using *Gnidia glauca* flower extract and were used as a chemocatalytic agent in the reduction of 4-nitrophenol to 4-aminophenol in the presence of sodium borohydride (Ghosh et al. 2012). The formation of gold nanoparticles was observed by the change in colour from yellow to dark red in the visible range of the spectrum from 450 to 600 nm (Fig. 17.3). Further, the UV–Vis spectrum of gold nanoparticles as a function of time showed that the reaction was completed within 20 min. It has been observed that the fabrication of gold nanoparticles starts 2 min after the interaction of *G. glauca* flower extract with $HAuCl_4$. This method of gold nanoparticle synthesis (Ghosh et al. 2012) was faster and more efficient than that reported earlier (Vankar and Bajpai 2010) which took about 2 h for the completion of the reaction.

Freshly cut leaves of *Hibiscus rosa-sinensis* were exposed to microwave heating for 3 min, and rapidly gold nanoparticles were synthesized. The SPR at 520 nm confirmed the synthesis of gold nanoparticles. TEM study exhibits the spherical-shaped nanoparticles in the size range of 16–30 nm. The nanoparticles' stability was proved during in vitro stability tests. It was found that alkaloids and flavonoids played a crucial role in the nanoparticle synthesis which was identified using the FTIR (Yasmin et al. 2014). In an experiment, leaf extract of two plants (*Magnolia kobus* and *Diopyros kaki*) were used to fabricate gold nanoparticles (Song et al. 2009). They observed that the reaction temperature and the leaf extract

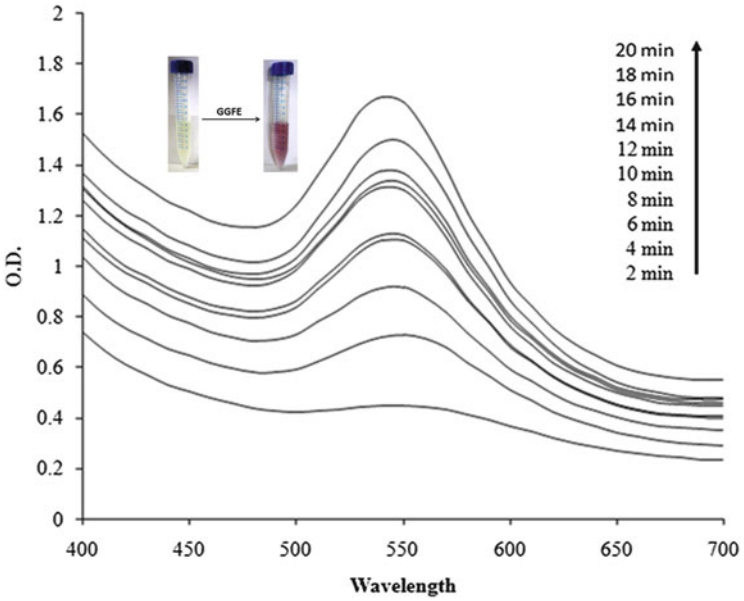

Fig. 17.3 UV–Vis spectra recorded as a function of reaction time of 1 mM chloroauric acid solution with *Gnidia glauca* flower extract at 40 °C (Ghosh et al. 2012)

concentration influenced the shape and the size of the gold nanoparticle formation. At higher temperatures and extract concentrations, smaller and mainly spherical nanoparticles were fabricated, whereas a variety of other morphologies in larger sizes were achieved at lower temperatures and extract concentrations. When an aqueous extract of *Dysosma pleiantha* was added to a solution of gold ions, it gave gold nanoparticles in a spherical shape of 127 nm in size (Karuppaiya et al. 2013). Interestingly, in this investigation gold nanoparticles were produced at boiling temperature. The average particle size of gold nanoparticles was inversely dependent on temperature in the range of 30–60 °C. Further, the antimetastatic activity of nanoparticles against human fibrosarcoma cancer cell line HT-1080 was tested. These gold nanoparticles had no toxic effect on cell proliferation. Moreover, these gold nanoparticles exhibited a high potential for the inhibition of cell migration of human fibrosarcoma cancer cell line HT-1080.

Pasca et al. (2014) reported that the reduction of Au (III) to Au(0) with plant extracts of *Angelica archangelica*, *Hamamelis virginiana* and *Hypericum perforatum* was rapid at room temperature, and for high dilutions of the plant extract, indicating the presence of a reducing substance in large amounts. In this study, the stability of the gold nanoparticles was more at high pH (8–10). It was suggested that the stabilization of nanoparticles was due to the adsorption of stabilizing substances present in the same plant extracts or perhaps also due to their oxidation products (quinones). Moreover, besides this extract, other substances are capable to mediate the self-assembly of nanoparticles. The best stability

was found by using *Angelica* extract, whereas self-aggregation tendency was higher in the presence of the *Hypericum* extract. Here a common trend was also observed; as such at a lower concentration of the plant extract, larger particles were formed. The tendency to self-aggregation was increased as a result of the dilution of protecting substances.

In several other studies, the size and shape of fabricated nanoparticles can be manipulated by adjusting the pH of the reaction mixtures. The main effect of the pH was in its ability to change the electrical charges of biomolecules which might have affected their capping and stabilizing abilities and subsequently the growth and production rate of nanoparticles. This may resulted in the favourable formation of nanoparticles of certain shapes at a specific pH range so that a greater stability can be obtained. For instance, in another study the pH-dependent fabrication of gold NPs by *Avena sativa* biomass was also performed (Armendariz et al. 2004) where face-centred cubic (fcc), tetrahedral, hexagonal, decahedral, icosahedral and irregular rod-shaped gold nanoparticles were produced. The yield was more at low pH (3). It was found that at higher pH, the gold nanoparticles of small size are produced. On the other hand, the rod-shaped gold nanoparticles were produced at all pH which has been reported to be formed mainly by electrodeposition in the presence of $KAuCl_4$ which produced $AuCl_4^-$ anion in water. Oat biomass has exhibited the ability to bind $AuCl_4^-$ and its subsequent reduction to gold nanoparticles. An available protein from *Macrotyloma uniflorum* was used to produce gold nanoparticles as capping and stabilizing agents (Aromal et al. 2012). UV–Vis spectrum of the produced gold nanoparticles in different extract quantities from 0.5 to 2 mL demonstrated a shift to shorter wavelengths, which shows the decrease in particle size, when the temperature was increased from room temperature to the 373 K at the same extract quantity SPR bands became broader and shifted to the longer wavelengths; this indicated the increment of particle size. Similarly, gold nanoparticles were synthesized using *Anacardium occidentale* extract where the pH of the reaction mixture was varied from 3 to 8 at room temperature. At pH 5 and 8, the SPR bands were broad, which shows that polydispersed nanoparticles were synthesized, while at pH 4, 6 and 7, the SPR bands were sharper; and at pH 6 a narrow band was recorded which was the characteristic of monodispersed spherical nanoparticles that was confirmed by TEM images (Sheny et al. 2011).

In a recent study, an enzymatic digestion process was developed for the simultaneous determination of nanoparticle size, distribution, particle concentration, and dissolved gold concentration in tomato plant tissues (Dan et al. 2015). The authors suggested that tomato plants can uptake gold nanoparticles of 40 nm diameter and transport them to various parts of the plant. It was suggested that the macerozyme R-10 enzyme can be used to extract the gold nanoparticles from the plant tissue system. Plant organ-dependent yield of gold nanoparticles has been also reported in *Cucurbita pepo* (Gonnelli et al. 2015). Gold nanoparticle one-pot synthesis was carried out at 40 °C for 30 min with diluted $HAuCl_4$. Shoot extracts produced a high number of spherical nanoparticles with lower size than gold nanoparticles as obtained from root extracts of *C. pepo*. Further, when root extracts grown in the

presence of Cu (II), Ag (I) or Au (III) produced nanoparticles with treatment-dependent shape, while using shoot extracts, this phenomenon was not recorded. This may be due to metal-imposed specific changes in the cell antioxidant pool, as the total polyphenol concentration in the extracts was correlated with the differences achieved in nanoparticle production. In another recent study, Tetgure et al. (2015) have reported the synthesis and properties of silver and gold nanoparticles using *Ficus racemosa* latex as reducing agent. The colloidal solutions of the nanoparticles exhibited characteristic absorption peaks in the UV-vis region of spectra containing a mixture of nanoparticles of varying size. As suggested by Tetgure et al. (2015) that under acidic condition COOH and NH_3+ groups of amino acids binds with nanoparticles but under basic conditions the COO^- and NH_2 of the same acids cannot bind the nanoparticles. It is very strange obsession of these workers who have hypothesized such imaginary chemical binding of nanoparticles with amino acids under acidic condition. First the nanoparticles are neutral atoms which can associate themselves under both acidic and basic conditions. Second only two charged species may be bonded such as a metal ion and an electron donor. They have mistaken the agglomeration with complexation.

17.3 Characterization of Synthesized Gold Nanoparticles

Characterization of nanoparticles is an important process to understand the reaction mechanism and its subsequent applications. Quite often used techniques for the characterization of nanoparticles, viz. UV–Vis spectroscopy, TEM, scanning electron microscopy (SEM), X-ray diffraction (XRD), FTIR spectroscopy, atomic force microscopy (AFM), energy-dispersive X-ray spectroscopy (EDX), dynamic light scattering (DLS) and zeta potential, are used. These techniques are useful for the determination of size, shape, surface modification, surface area, crystallinity and dispersity of nanoparticles. Generally, UV–visible spectroscopy analysis is used initially for the characterization of noble metallic nanoparticles including gold. Gold nanoparticles have strong absorption in the visible region with the maximum in the range of 500–600 nm due to the SPR phenomenon. This is attributed to the collective oscillation of free conduction electrons induced by an interacting electromagnetic field with the concerned metallic nanoparticles. The appearance of extract colour in red, purple, violet or pink-ruby red due to excitation of SPR vibration in the above-mentioned wavelength confirms the production of gold nanoparticles. For instance, *Solanum melongena* leaf extract leads to the production of a higher quantity of gold nanoparticles followed by *Datura metel* and *Carica papaya* (Rajasekharreddy et al. 2010). When $HAuCl_4$ solution was exposed to *Tridax procumbens*, *Jatropha curcas*, *Calotropis gigantea*, *S. melongena*, *D. metel*, *C. papaya* and *Citrus aurantium* leaf extract solutions exhibited purple colours in the reaction mixture which indicated the formation of gold nanoparticles (Fig. 17.4a–g). For the size and shape of the synthesized nanoparticles, SPR band is able to provide useful information. SPR wavelength variations with the variations

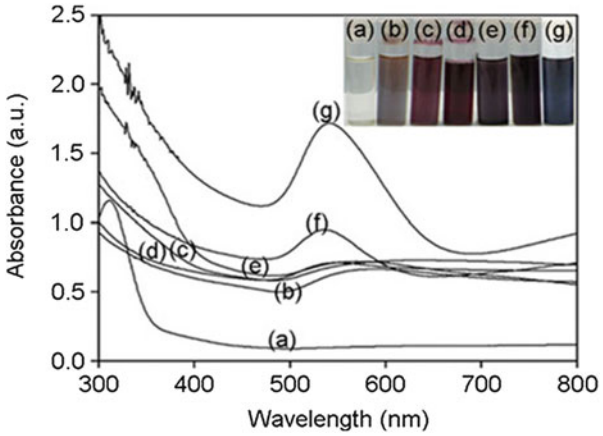

Fig. 17.4 UV–Vis absorption spectra of colloidal gold nanoparticles synthesized using (**a**) *Calotropis gigantea*, (**b**) *Jatropha curcas*, (**c**) *Tridax procumbens*, (**d**) *Citrus aurantium*, (**e**) *Carica papaya*, (**f**) *Datura metel* and (**g**) *Solanum melongena* leaf extracts (the *inset* of the figure shows glass vials of the gold nanoparticle solution formed at the end of the reaction) (Rajasekharreddy et al. 2010)

in particle size in the extract of various plant species have already been established by different workers as with *Cinnamomum camphora* (Huang et al. 2007), *Camellia sinensis* (Vilchis-Nestor et al. 2008), cypress (Noruzi et al. 2012), *Artocarpus heterophyllus* (Jiang et al. 2013), *Hibiscus rosa-sinensis* (Yasmin et al. 2014) and *Citrus maxima* (Yu et al. 2016).

Microscopic techniques, for example, SEM, TEM and AFM, are mostly used for morphological studies of the concerned nanoparticles. The use of these microscopic techniques in morphological studies of nanoparticles has been mentioned previously. TEM is used for greater magnification and resolution than SEM. TEM is also used to differentiate the crystalline structures from amorphous structures using the electron diffraction pattern for a selected area (SAED) (Kasthuri et al. 2009; Tripathi et al. 2016) (Fig. 17.5). AFM is used to study the shape of gold nanoparticles (Ghodake et al. 2010; Pasca et al. 2014).

The XRD technique is used to establish the structural information of crystalline metallic nanoparticles and confirms the formation of zero-valent nanoparticles (Jun et al. 2014). X-rays are electromagnetic radiation with typical photon energies in the range 100 eV–100 keV. Only short-wavelength X-rays in the range of a few angstroms to 0.1 Å (1–120 keV) are used for diffraction applications. Since the X-ray wavelength is comparable to the atom size, they are perfectly suitable for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays are able to penetrate deep into the materials and provide valuable information about the bulk structure (Putnam et al. 2007). The XRD technique is also used to calculate the crystallite sizes by the use of the Debye–Scherrer equation (Dubey et al. 2010b). Reports are available on the use of

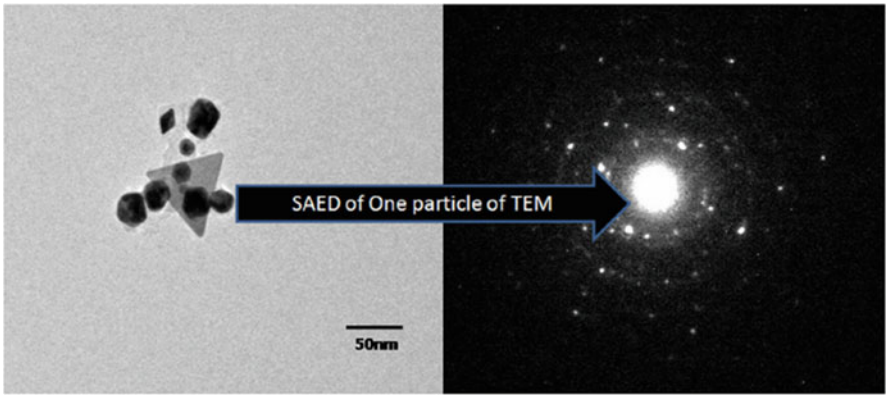

Fig. 17.5 TEM and SAED image showing the size, morphology and texture of gold nanoparticles as obtained from the aqueous leaf extract of *Achyranthes aspera* and gold chloride solution (Tripathi et al. 2016)

XRD pattern/peaks during fabrication of gold nanoparticles (Rajasekharreddy et al. 2010; Jun et al. 2014; Yu et al. 2016).

FTIR spectroscopy is used to measure infrared intensity against wavelength (wave number) of light. It is used to identify the biomolecules involved in the reduction and formation of the concerned nanoparticles. On the basis of wave number, infrared light can be considered as far infrared (4–400 cm^{-1}), mid infrared (400–4000 cm^{-1}) and near infrared (4000–14,000 cm^{-1}). Several studies have compared the FTIR spectrum during fabrication of gold nanoparticles and produced the information about the reducing and capping agents such as proteins, polysaccharides, flavonoids, terpenoids, phenols, ascorbic acids and so on. For instance, FTIR pattern of the gold nanoparticles synthesized using *C. maxima* fruit extracts exhibited bands at 617, 1125, 1376, 1658 and 3278 cm^{-1} (Yu et al. 2016). Aromal et al. (2012) have reported the presence of intense band at 1729 and 1642 cm^{-1} which indicates that the gold nanoparticles are probably bound to proteins present in the aqueous extract of *M. uniflorum* through amine group. The FTIR spectra comparison of plants before and after reaction, the functional groups, such as—OCH_3 of phyllanthin (Kasthuri et al. 2009) and polyols of the *C. camphora* leaf extract (Huang et al. 2007) were identified. In another study, Jiang et al. (2013) demonstrated that the FTIR spectra (Fig. 17.6a) of the biomass of *A. heterophyllus* leaf extract before reduction exhibits bands at 3402, 2931, 1606, 1518, 1402, 1260 and 1076 cm^{-1}. The bands at 3402, 1606 and 1518 cm^{-1} were given to the aromatic hydroxyl and benzene ring, which indicated that there are phenols in the extract (Andrei et al. 2012). Bands at 2931 and 1402 cm^{-1} are stretching vibrations of the methylene and deformation vibration of the methyl, while bands at 1260, 1113 and 1076 cm^{-1} are assigned to epoxy bond, semi-acetal and primary alcohol indicated the presence of sugars in the extract. Further, FTIR spectra of the biomass *A. heterophyllus* leaf extract after reduction (Fig. 17.6b) exhibits analogous bands at 2931, 1615, 1509, 1385 and 1068 cm^{-1}. The main variation between the two

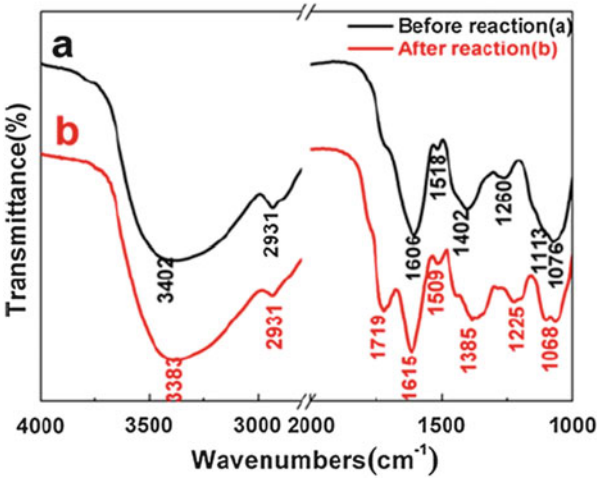

Fig. 17.6 FTIR spectra of the biomass *Artocarpus heterophyllus* leaf extract before (**a**) and after (**b**) reaction (biomass, 2.965 mg mL^{-1}; HAuCl4: 1 mM; 30 °C; 180 min) (Jiang et al. 2013)

waves lies in the fact that, original peaks at 3402 and 1260 cm^{-1} disappeared, whereas new peaks at 3383, 1719 and 1225 cm^{-1} appeared after the reaction, which meant that the epoxy band was broken and aromatic hydroxyl was oxidized to carbonyl. Hence, these FTIR studies suggested that the reducing sugars and the phenols are responsible for Au(III) reduction and gold nanoparticle stabilization.

Raman spectroscopy is a molecular spectroscopy that is observed as inelastically scattered light that allows for the interrogation and identification of vibrational (phonon) states of molecules. Thus, this spectroscopy provides an invaluable analytical tool for molecular finger printing as well as monitoring changes in molecular bond structure. In this technique, very little sample preparation and a rapid, non-destructive optical spectrum are easily achieved. Raman spectra are normally carried out with green, red or near-infrared lasers. Gold nanoparticles enhance the intensity of Raman scattering of adjacent molecules. Thus, they are usually employed in surface-enhanced Raman scattering (SERS) for the detection and quantitative study of Raman active materials such as some organic and inorganic species at low concentration. The uses of SERS in new material characterization, identification and their applications have been already reported (Dieringer et al. 2006; Alvarez-Puebla et al. 2007; Kalmodia et al. 2013; Sun et al. 2014; Prasad et al. 2016). NMR spectroscopy has also been used to confirm the functionalization of gold nanoparticles (Shankar et al. 2004a; Das et al. 2011).

Zeta potential is a potential difference between the two suspended particles present in colloidal suspension. It is a physical property which confirms the stability of nanoparticles. Zeta potential values may be positive or negative but values above than −30 mV or +30 mV favour the good quality and stability of nanoparticles and such nanoparticles can be stored for a longer period of time. Zeta potential strongly depends on the pH of the solution. For instance, in a fixed temperature (25 °C) at pH 6, zeta potential is −9.62 mV that exhibits poor quality, unstable gold nanoparticles. At pH 7 zeta potential value is −25.7 mV, with zeta deviation

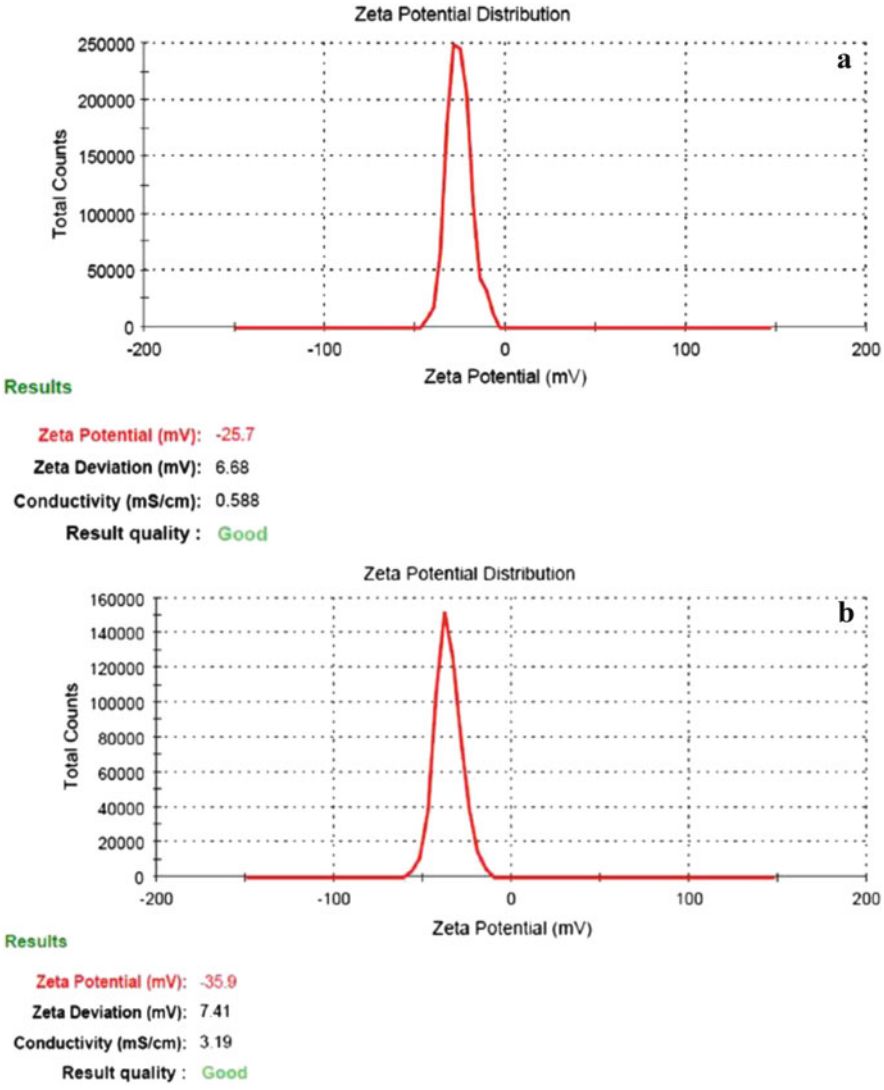

Fig. 17.7 Zeta potential value and zeta potential distribution graph of *Achyranthes aspera* gold nanoparticles at pH 7 (**a**) and 10 (**b**) (Tripathi et al. 2016)

6.68 mV and conductivity 0.588 mS cm^{-1} which represents good quality but unstable nanoparticles (Fig. 17.7a). Whereas at pH 10 zeta potential value is –35.9 mV, with zeta deviation 7.41 mV and conductivity 3.19 mS cm^{-1} which exhibits good quality and comparatively better stability of gold nanoparticles (Fig. 17.7b). Tripathi et al. (2016) claimed that the gold nanoparticles that have zeta potential of −35.9 mV can be stored for up to 2 months without compromising their quality and stability.

17.4 Applications of Gold Nanoparticles

Surprisingly, the applications of nanoparticles have a long history. Though, in recent years different metal nanoparticles with unique properties have been synthesized and applied in many research areas. Among these, gold nanoparticles have attracted intense interests due to their unique optical and electrical properties, high stability and good biocompatibility. Since the ancient civilizations, gold has been used to treat various types of diseases such as smallpox, skin ulcers, syphilis and measles (Tanaka 1999; Huaizhi and Yuantao 2001; Richards et al. 2002; Gielen and Tiekink 2005; Kumar 2007; Chen et al. 2008). Moreover, the Romans in the fourth century used gold for adding a striking red colour to glass (Lycurgus Cup); it appears with a green colour in daylight but changes to red, when illuminated from the inside (Leonhardt 2007; Freestone et al. 2007) (Fig. 17.8). Currently, advances in synthesis and surface functionalization of nanoparticles (effective manipulation) have led to numerous promising and diverse applications of gold nanoparticles as mentioned in Fig. 17.2. Gold nanoparticles are competent of delivering large biomolecules, without restricting themselves as carriers of only small molecular drugs. Facile tunable size and functionality make them a valuable scaffold for efficient recognition and delivery of biomolecules. Gold nanoparticles have shown success in the delivery of peptides, proteins or nucleic acids like DNA or RNA (Verma et al. 2004; Bhumkar et al. 2007; Ghosh et al. 2008; Rana et al. 2012; Ding et al. 2014). They were used as a carrier in the preparation of the anticancer agent, paclitaxel (Gibson et al. 2007), and attached with vascular endothelial growth factor antibodies which are employed in treating B-chronic lymphocytic leukaemia (Mukherjee et al. 2007). Biosensors are generally defined as sensors that consist of biological recognition elements, often called bioreceptors or transducers (Vo-Dinh and Cullum 2000). SERS by gold nanoparticles has been used to identify tumours in cancer research (Huang and El-Sayed 2010), immunoassays (Grubisha et al. 2003; Neng et al. 2010), study of living cells (Kneipp et al. 2002), detection of Alzheimer's disease markers (Neely et al. 2009), determination

Fig. 17.8 The Lycurgus Cup in reflected (*left*) and in transmitted (*right*) light. © Trustees of the British Museum

of protease activity (Guarise et al. 2006) and several other purposes (Dykman and Khlebtsov 2012).

Gold nanoparticles possess catalytic activity and are thus widely used for selective reactions at low temperature such as the water–gas shift reaction and selective oxidation of carbon monoxide (Andreeva 2002; Grisel et al. 2002; Hutchings and Haruta 2005), methanol (Hernández et al. 2006), glycerol (Carrettin et al. 2002), hydrogenation of unsaturated materials (Claus et al. 2000), reduction of aromatic nitro compounds (Kundu et al. 2009) and a toxic pollutant 4-nitrophenol to 4-aminophenol (Sharma et al. 2007; Ghosh et al. 2012; Yu et al. 2016).

Gold nanoparticles have shown antimicrobial properties. Cationic and hydrophobic functionalized gold nanoparticles are found to effectively suppress the growth of 11 clinical multidrug-resistant isolates, including both Gram-negative and Gram-positive bacteria (Li et al. 2014). The nanogold bioconjugate exhibits antimicrobial activity against several Gram-negative and Gram-positive pathogenic bacteria as well as *Saccharomyces cerevisiae* and *Candida albicans* (Das et al. 2009). The synthesized silver and gold nanoparticles from *Mentha piperita* exhibited a strong antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* (Ali et al. 2011). In addition, the antibacterial activities of honey-mediated gold and silver nanoparticles have been observed (Sreelakshmi et al. 2011).

Several uses of gold nanoparticles, as biosensor substrates, have been reported (Liu and Lu 2003; Luo et al. 2004; Li et al. 2010). For instance, they have been utilized in the biosensor design to improve the performance for the detection of infectious diseases and biothreats (Lin et al. 2013). Gold nanoparticle-based sensors are useful to detect toxins, heavy metals and inorganic and organic pollutants in water rapidly with high sensitivity, and thus they are believed to play an important role in environmental cleaning and monitoring. They have been used in chemical sensing such as potassium (Lin et al. 2002), lithium (Obare et al. 2002) and toxic heavy metals like mercury, lead and cadmium (Kim et al. 2001). This was demonstrated by using surface-engineered gold nanoparticles. Gold nanoparticles are also useful for the removal of heavy metals by the formation of alloys with varying composition, for instance, Au_3Hg, AuHg and $AuHg_3$ phases, and therefore they can be utilized for the removal of Hg ions from the contaminated water (Pradeep and Anshup 2009). Gold nanoparticle-based sensor for the selective detection of Cr^{3+} in aqueous solution, in the presence of 15 other metal ions, has been demonstrated (Dang et al. 2009). They can also be used for the detection and removal of organic compounds such as pesticides (Han et al. 2003) endosulfan, malathion and chlorpyrifos (Nair et al. 2003). Sulphur-containing compounds bind with gold nanoparticles, causing a change in the suspension colour (to purple). Aggregation of the endosulfan bond gold nanoparticles ultimately occurs, which basically removes the endosulfan into a concentrated, solid form. In the availability of methanol co-solvent, Bootharaju and Pradeep (2012) found the decomposition of chlorpyrifos at room temperature in the presence of gold nanoparticles. Salt-induced aggregation of gold nanoparticles was also used for the detection of pesticides in drinking water at low concentration (Burns et al. 2006). Moreover,

Gupta and Kulkarni (2011) have shown the removal of diesel oil droplets floating on water through swelling and absorption of the gold nanoparticle composite. Application of fabricated gold nanoparticles in plant growth and production has shown significant promising potential. Both beneficial and harmful response of gold nanoparticles in plant system has been reported (Husen and Siddiqi 2014b; Siddiqi and Husen 2016b). Gold nanoparticles enter into plant system by a size-dependent mechanism where they may trigger the growth/biomass or inhibit the growth by leading an imbalance in physiological, biochemical and molecular processes; and producing oxidative stress. They exhibited inhibition of reactive oxygen species which suggests the free radical scavenging ability of gold nanoparticle. In addition, their exposure has also altered microRNA and gene expression in plants. It has been suggested that the gold nanoparticles may be applied in fruiting plants to increase the quality and quantity of the fruits and vegetable (Siddiqi and Husen 2016b).

17.5 Conclusion

Owing to reach plant biodiversity, the phytosynthesis of gold nanoparticles is able to create facile, eco-friendly, inexpensive and stable nanoparticles in comparison to physical and chemical methods. Available biomolecules in plant systems played a significant role during bioreduction process. Some studies have shown control over the shape and size of gold nanoparticles by adjustment of concentration of plant extract or biomass, concentration of metal salt, incubation/reaction time, temperature and pH of the solution. However, this fabrication mechanism is not fully understood and is still in its infancy stage. Development of a highly controllable fabrication approach is desirable. The stability of synthesized gold nanoparticles is another concern to achieve a longer time/duration and maximum practical application. Thus, more experiments are anticipated to elucidate the reduction mechanism to control well-defined size and shape and the stability of gold nanoparticles. The high potential applications of gold nanoparticles in various sectors are worth exploring specially in biomedicine and catalysis. The recent use of engineered gold nanoparticles in drug and gene delivery, catalytic activity, infectious diseases control and environmental monitoring is an established fact. At the same time, the unique physicochemical properties of gold and other metallic nanoparticles are of great concern regarding the potential adverse effects as arisen with their increasing production, use and disposal which unavoidably lead to ecological risk. In addition to this, another key issue to consider in the use of gold nanoparticles is to calculate the cost to see as if it is economically viable.

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