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Biosynthesis of Gold Nanoparticles (Green-Gold) Using Leaf Extract of *Terminalia Catappa*

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Abstract: The synthesis of eco-friendly nanoparticles is evergreen branch of nanoscience for biomedical application. Low cost of synthesis and non toxicity are main features make it more attractive potential option for biomedical field and elsewhere. Here, we report the synthesis of gold nanoparticles in aqueous medium using *Terminalia catappa* (Almond) leaf extract as the reducing and stabilizing agent. On treating chloroauric acid solutions with *Terminalia catappa* (TC) leaf extract rapid reduction of chloroaurate ions is observed leading to the formation of highly stable gold nanoparticles in solution. TEM analysis of the gold nanoparticles indicated that they ranged in size from 10 to 35 nm with average size of 21.9 nm.

Keywords: Biosynthesis, *Terminalia catappa*, Gold nanoparticles, Green-gold.

Introduction

Currently, there is growing need to develop eco-friendly and body benign nanoparticle synthesis processes without use of toxic chemicals in the synthesis protocols to avoid adverse effects in biomedical applications. Obviously, researchers in this field paid their attention towards the use of biological systems for the synthesis of biocompatible metal and semiconductor nanostructures. Some well-known examples of bio-organisms synthesizing inorganic materials include magnetotactic bacteria (synthesizing magnetite nanoparticles)[1] diatoms (synthesizing siliceous materials)[2] and *S*-layer bacteria (producing gypsum and calcium carbonate layers)[3].

Many biotechnological applications such as remediation of toxic metals employ microorganisms such as bacteria[4] and yeast[5]. Nair and Pradeep[6] have synthesized nano-crystals of gold, silver and their alloys by reaction of the corresponding metal ions within cells of lactic acid bacteria present in buttermilk. The bacteria[7] and algae[8] are exploited for synthesis of gold nanoparticle.

The extra cellular synthesis of gold nanoparticles of about 8 nm diameter has also been reported by using the alkalothermophilic actinomycete *Thermomonospora* sp[9]. As can be seen from the above, the use of microorganisms in the deliberate and controlled synthesis of nanoparticles is a relatively new and exciting area of research with considerable potential for development. Recently synthesis of Au and Ag nanoparticles using extracts of cinnamomum camphora leaf[10], phyllanthin[11] and edible mushroom[12] as a reducing and capping agent has been reported.

While the microorganisms such as bacteria, actinomycete and fungi continue to be investigated in metal nanoparticle synthesis, the use of parts of whole plants, similarly in nanoparticle synthesis methodologies is an exciting possibility that is relatively unexplored and underexploited. Using plants for synthesis of nanoparticles could be advantageous over other environmentally benign biological processes by eliminating the elaborate process of maintaining cell cultures. It can also be suitably scaled up for large-scale synthesis of nanoparticles. Recently, Jose-Yacaman and co-workers[13] demonstrated the synthesis of gold and silver nanoparticles within live alfalfa plants in solid media. Moreover, agricultural biomass has been used to reduce Cr(VI) to Cr(III) ions[14] indicating that biological methods can be very efficient in decontaminating polluted waters and soil polluted with heavy metal ions.

In our earlier reports, synthesis of gold nanoparticles have been shown by the reduction of aqueous $AuCl_4^-$ ions using extracts from *Emblica officinalis* (Indian Gooseberry) fruit[15] and *Tamarindus indica*[16] leaf. Recently, we had demonstrated the biological synthesis of triangular gold nanoprisms by a single step, room temperature reduction of aqueous chloroaurate ions by the extract of the plant, lemongrass[17]. There is still much scope for improvement in bio-based methods for metal nanoparticle synthesis, particularly in relation to improving the monodispersity of the nanoparticles and modulating their size and shape, as well as in reducing the time required for nanoparticle synthesis. On a more fundamental level, it would be interesting to study the nature of nanoparticles formed using extracts from different parts of a plant. The main idea behind selection of TC extract is due to its anticancer[18], antibacterial[19] and antioxidant activities[20-22],

In this paper we demonstrate method for the synthesis of gold nanoparticles by the reduction of aqueous chloroaurate ions by using *Terminalia catappa* leaf extract.

Experimental

Reagents and Chemicals

Tetrachloroauric acid ($HAuCl_4.XH_2O$) was obtained from Sigma Aldrich. Freshly prepared double distilled water was used through out the experimental work.

Biological synthesis of gold nanoparticles

The broth used for the reduction of Au^{3+} ions to Au^0 was prepared by taking 10 g of thoroughly washed and finely cut *Terminalia catappa* leaves in a 500 mL Erlenmeyer flasks with 40 mL of sterile distilled water and then was boiled it for 15 min. In a typical experiment, 0.2 mL of broth was added to 50 mL of 10^{-3} M aqueous chloroauric acid ($HAuCl_4$) solution. Within an hour (50 minutes) cherry red solution was obtained.

UV-Vis spectroscopy studies

UV-Vis spectroscopy measurement of the *Terminalia catappa* leaf extract reduced gold nanotriangles was carried out on a JASCO dual-beam spectrophotometer (model V-570) operated at a resolution of 1 nm.

X-ray diffraction (XRD) measurement

XRD measurements of the bioreduced chloroauric acid solution drop-coated on glass were done on a Phillips PW 1830 instrument operating at a voltage of 40 KV and current of 20 mA with Cu Kα radiation.

Fourier transform infrared (FTIR) spectroscopy measurements

For FTIR spectroscopy measurements, drop coated samples on Si (111) wafers were prepared. After complete reduction of $AuCl_4^-$ ions by the *Terminalia catappa* leaf broth and formation of gold nanoparticles was centrifuged at 9000 rpm for 10 min to isolate the gold nanoparticles from free proteins or other compounds present in the solution. The gold nanoparticle pellets obtained after centrifugation were redispersed in water prior to FTIR analysis centrifuged again at 9000 rpm for 10 min to isolate the gold nanoparticles from traces of free proteins or other compounds present in the solution if any. FTIR measurements of TC leaf extract reduced gold nanoparticles were carried out on a Perkin-Elmer FTIR Spectrum One spectrophotometer in the diffuse reflectance mode operating at a resolution of 4 cm^{-1}.

TEM measurements

TEM samples of the gold nanoparticles synthesized by the biological reduction were prepared by placing a drop over carbon coated copper grids and allowing the solvent to evaporate. TEM measurements were performed on a JEOL model 1200EX instrument operated at an accelerating voltage at 80 kV.

Results and Discussion

The reduction of aqueous $AuCl_4^{--}$ ions during reaction with the TC leaf extract may be easily followed by UV-vis spectroscopy. Figure 1A shows the UV-vis absorption spectra recorded from the TC leaf extract (curve 1), as-prepared aqueous gold nanoparticle solution (curve 2), a strong resonance at ca. 524 nm is clearly seen in curve 2 and arises due to the excitation of surface plasmon vibrations in the gold nanoparticles[23].

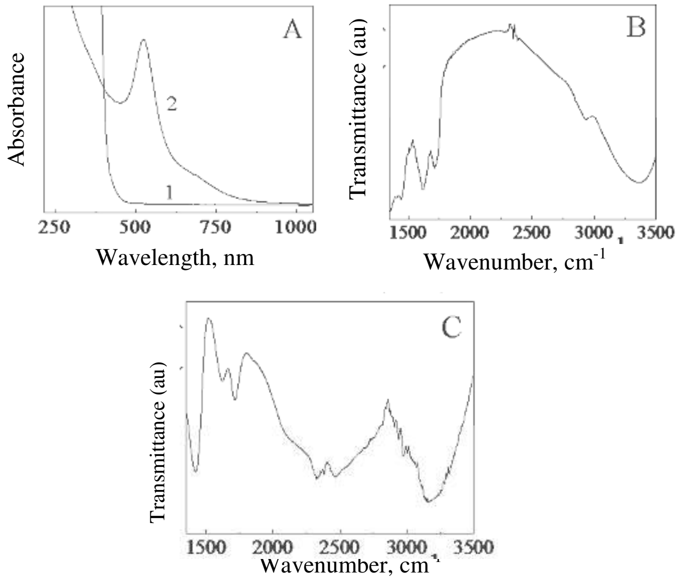

Figure 1. (A) UV-Vis absorption spectra recorded from TC leaf extract (1), TC leaf extract-reduced gold nanoparticles (2); FTIR spectra recorded (B) from pure TC leaf extract and (C) from TC extract-reduced gold.

It should be noted here that there is no time-dependent change in the UV – vis absorption spectra. Curve 2 in Figure 1A clearly indicating that the gold nanoparticles in aqueous phase are extremely stable with no precipitation observed even after four months. The stability for such a long period seems to be due to antimicrobial[19] and antioxidant[20-22] properties of TC leaf extract.

FTIR measurements were carried out to identify the possible biomolecules in the TC leaf extract responsible for the reduction of $AuCl_4^-$ ions and also the capping agents responsible for the stability of the biogenic nanoparticle solution. Chen *at al*[24] reported that leaves of TC contains 21% tannin, whereas Rayudu and Rajdurai[25] analyzed the polyphenols and carboxylic compounds of TC. Figure 1B represents the FTIR spectrum of TC leaf extract which shows prominent absorption bands at 1718 cm^{-1}, 1441 cm^{-1} and 3372 cm^{-1}. The shoulder at 1718 cm^{-1} is characteristic of carbonyl stretch vibrations from carboxylic acid and phenols, while the stretch at 1441 arises due to the C-O stretching and O-H deformation possibly from the acid groups present in the TC leaf extract[26, 27]. The broad stretching at 3372 cm^{-1} arises due to the free O-H groups present in the phenols. Figure 1C represents the FTIR spectrum of the TC leaf extract reduced gold with the absorption bands at 1420 cm^{-1}, 1715 cm^{-1} and 3145 cm^{-1}. The shift in the carbonyl stretch frequency (1718 cm^{-1}) to lower wavenumbers (1715 cm^{-1}) followed by the disappearance of the 1718 cm^{-1} resonance may be due to its binding with the gold nanoparticle surface. The shift in the C-O stretching and O-H deformation frequency (1441 cm^{-1}) to lower wavenumbers (1420 cm^{-1}) followed by the disappearance of the 1441 cm^{-1} resonance indicate the facilitation of the binding of O-H group of phenols with the gold nanoparticle surface. In addition to above supportive evidence the 3372 cm^{-1} feature shifts to 3145 cm^{-1} due to the binding of the hydroxyl group with gold nanoparticle surface[26].

Figure 2A and 2B show a TEM and low magnification TEM image recorded from the biologically synthesized gold nanoparticles at the end of the reaction with TC leaf extract respectively, while Figure 2C is a plot of particle size distribution (PSD) histogram measured from an analysis of 120 particles from Figure 2A. The TEM image shows that the gold nanoparticles are predominantly spherical in morphology with their size ranging from 10 to 35 nm with an average size of about 21.9 nm. A Gaussian fit to the PSD histogram yielded a particle size of 21.9 ± 2 nm.

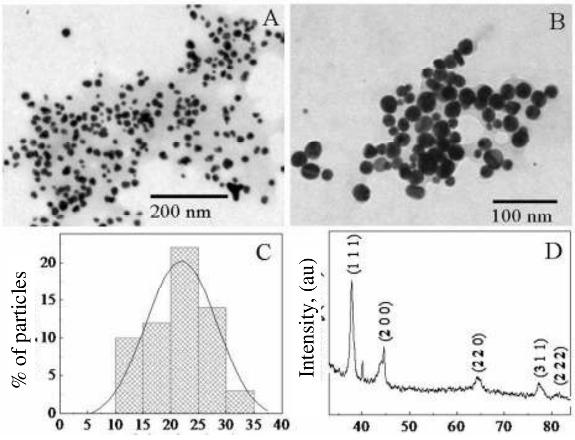

Figure 2. Representative TEM images of TC leaf extract-reduced gold nanoparticles at low magnification (A) and at higher magnification (B). The lower panels in the image (A) shows the corresponding particle size distribution histograms (C). The solid lines in the lower panels is Gaussian fits to the histogram. (D) XRD pattern of a solution-cast film of the TC leaf extract-reduced gold nanotriangles deposited on a glass substrate. The Bragg reflections are identified in the XRD pattern.

The formation of gold nanoparticles synthesized using TC leaf extract was further supported by X-ray diffraction (XRD) measurements (Figure 2D). The Bragg reflections corresponding to the (111), (200), (220), (311) and (222) sets of lattice planes are observed that may be indexed on the basis of the fcc structure of gold. The (200), (220), (311) and (222) Bragg reflections are weak and considerably broadened relative to the intense (111) reflection. This interesting feature indicates that gold nanocrystals are in the film are predominantly (111)-oriented.

The antibacterial[19] and antioxidant[20-22] properties of biomolecules present in the TC leaf extract have facilitated excellent stability of the nanoparticles. The size of the nanoparticles being in the range 10 - 35 nm with average size of 21.9 nm makes circulation into blood vessels feasible. In addition to the size and stability, the anticancer[18], antibacterial[19], antioxidant[20-2] properties of TC leaf extract could have important application in the use of the biogenic gold nanoparticles in cancer therapy, and is currently being pursued.

Conclusion

The rapid synthesis of stable gold nanoparticles using TC leaf extract has been demonstrated. The reduction of the metal ions and the stabilization of the Au nanoparticles is believed to occur by the various acids and hydrolysable tannins present in the TC leaf. The nanoparticles are extremely stable with time. The anticancer, antibacterial and antioxidant properties of TC leaf extract could be exploited in the use of the biogenic gold nanoparticles in cancer therapy.

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