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Green synthesis of gold nanoparticles from *Combretum indicum* and their characterization

Sachchidanand Soaham Gupta[1],Pooja Patanjali[1], Neeraj Kumar Mishra[2], Amit Kumar[3],Indu Chopra[4] & Rajeev Singh[1]*

[1]MaterialsResearch Laboratory, Department of Chemistry, Atma Ram Sanatan Dharma College, University of Delhi 110 021, India

[2]School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110 067, India

[3]School of Materials Science, Energy and Environment Area, International Research Centre for Sustainable Materials, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa, 923-1292, Japan

[4]Division of Soil Science and Agricultural Chemistry, ICAR-Indian Agricultural Research Institute, New Delhi 110 012, India

E-mail: rajeev@arsd.du.ac.in

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Green synthesis of gold nanoparticles (AuNPs) facilitated by the use of an aqueous petal extract of the medicinal plant *Combretum indicum* (*Madhumalti*) as a bio-reducing agent has been performed in this work. In the absence of ammonia, the average diameter of synthesised gold nanoparticles ranged from 41nm to 79.40 nm whereas the range is 11.856 nm to 49.2 nm in the presence of ammonia. The formation of AuNPs is mediated by time that is monitored by Surface Plasmon behaviour using UV-Vis Spectroscopy at different stirring time intervals. The reaction shows a significant increase in absorbance with time with an absorbance peak in the range of 530-570 nm after one hour of stirring. Synthesis of nanoparticles is confirmed by the change of colour of auric chloride from yellow to dark brown. Synthesized AuNPs have been characterized by dynamic light scattering (DLS), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX).

Keywords: Gold nanoparticles, Green synthesis, Plant extract, Surface plasmon resonance

Significant advancements in Chemistry have emphasised the relevance of developing a robust, environmentally friendly method for the synthesis of metal nanoparticles. Metal nanoparticles have been prepared using several methods such as chemical reduction[1], sono-electrochemical[2,3], photochemical using UV irradiation[4,5], sono-chemical[6], seed-mediated growth method[7]. Activities of these biosynthesised nanoparticles have been studied against various microorganisms such as bacteria, actinomycetes and fungi[8]. Nanoparticle synthesis using single step green method is an exciting possibility and is relatively unexplored and underexploited. In this method phytochemicals such as terpenoids, flavones, ketones, amides, aldehydes in the plant extract act as reducing agent has many advantages, which comprise quick metal ion reduction to base metal, facile scaling, and simplicity of synthesis at low temperature and mild pressure[9].

For many years, this superb vine of *Combretum indicum*, has found usage as an Indian herbal medicine in Ayurveda and the Thai traditional system of medicine. Since time immemorial, concoctions of the root, seed, and petals have been employed in a variety of cures to treat a variety of diseases[9]. The flower extracts of the plant contain linalool oxides (furanoid), quinole carbonitrile, gallic acid, and flavonoids (quercetin and rutin)[10]. The petal extract of the plant shows vivid immunomodulatory activity[11], inhibition towards acetylcholinesterase (AChE)[12], and isknown to cure the symptoms of spermatorrhoea, weakness, leucorrhoea, diabetes etc. Gold nanoparticles (AuNPs) have gained an important space in nanoparticle research due to their distinctive and tuneable Surface Plasmon Resonance (SPR).Gold nanoparticle-based sensors have been found useful to detect toxins, heavy metals[13], inorganic and organic pollutants[14] in water rapidly with high sensitivity. Hence, synthesis of AuNPs by economical method can lead to its better utilization in environmental monitoring of contaminants in different environmental compartments.

In this study, we carried out rapid synthesis of gold nanoparticles using the aqueous petal extract of *Combretum indicum* by the reduction of $AuCl_4^-$ salt to Au. The size, morphology and shape have been

controlled by altering the reaction conditions. The effects of reaction conditions such as the reaction time at different concentration of aqueous ammonia on the particle size and surface morphology of the synthesized Au nanoparticles have also been investigated.

Experimental Section

Methods

Absorption spectra of the samples were obtained using a UV–vis spectrophotometer (*UV SPECORD 250* spectrophotometer). Photoluminescence (PL) spectra of the samples were obtained using photoluminescence spectrophotometer (HORIBAYVON spectrometer) at an excitation wavelength of 450 nm with Argon laser as the photon source and a photomultiplier tube (PMT) as the detector; DI water was used as the reference. Scanning Electron Microscopy: The samples from the maximum time point of production of gold nanoparticles were mounted on specimen stubs with double-sided adhesive tape and coated with gold to avoid charging and examined under *SEM (*JEOL at 200 kV*)* to investigate the morphology and the particle size of the product. Dynamic light scattering (DLS) analysis was carried out on RINA GmbH Laser-spectroscatter 201 to get the information about particle size distribution of the synthesized nanoparticles. Energy Dispersive X-ray Spectroscopy (EDX) was carried out on EDAX EVO-18 at 15 K Volt.

Synthesis of Plant Extract

The plant extract was synthesised as mentioned in our previous report[9]. Flowers of *C. indicum* were collected and rinsed with deionized water to remove any dust before being used. Petals were removed with care to avoid any green portions of the anther and/or the thalamus, and they were left at room temperature overnight to dry completely properly. The dried petals were placed in a Soxhlet apparatus with 200 mL of deionized water, and the contents were refluxed for 4 h. The resulting aqueous petal extract was filtered through celite. It was diluted to a volume of 500 mL and then stored in a deep freezer (at 0°C.).

Bio-synthesis of Nanoparticles

Petal extract (5 mL) was added dropwise to 10mL of a 10 mM $HAuCl_4$ solution in a round bottom flask under nitrogen atmosphere. Subsequently, 5 mL of aqueous ammonia (25% NH_3) was added, followed by addition of the desired amount of deionized water to get the final volume up to 50 mL. The solutions were stirred for various time intervals, viz 0h, 1h, and 2h. The procedure is then repeated times with three different solutions without the addition of ammonia and at the same ti me intervals.The bioreduction of $AuCl_4^-$ ions in the solution was monitored by periodically sampling aquilots (0.1mL) of solution and analysing the UV-Vis spectra of the samples at predefined time intervals (Fig. 1).

Results and Discussion

The addition of *C. indicum* petal extract to an aqueous solution of $AuCl_4^-$ ions resulted in a change in colour from light brown to dark brown. The intensity of the colour also increased as the reaction mixture was stirred for a longer period of time. The colour change occurs due to excitation of Surface Plasmon Resonance (SPR) in the gold nanoparticles[15]. This reduction of gold ions with the plant extract yields spherical, triangular, and hexagonal nanoparticles of varied sizes (from 10 to 300 nm).

UV-Vis Spectroscopy

The collective oscillation of conducting electrons in metals occurs in resonance with electromagnetic radiation, at certain wavelengths. Gold nanoparticles are known to exhibit Surface Plasmon Resonance (SPR) phenomenon due to this attribute. The SPR bands of nanoparticles are dependent on a variety of characteristics, including their size, shape, and the environment. The UV–vis spectra of gold nanoparticles through plant extract with (Fig. 2a) and without (Fig. 2b) in the presence of ammonia has been performed at different time intervals of stirring of the reaction mixture. The SPR band of gold appears initially at 550nm and extends to 580nm in wavelength. With increasing time, the plasmon bands of AuNPs grow broader, with a longer tail in the longer wavelength regions of the spectra. This is due to in-plane SPR excitation and specifies significant anisotropy in the shape of AuNPs.

Photoluminescence Spectra

It has been reported that nano-sized gold and silver particles exhibit visible photoluminescence[9,16-18]. Photoluminescence of noble metals can be seen as the

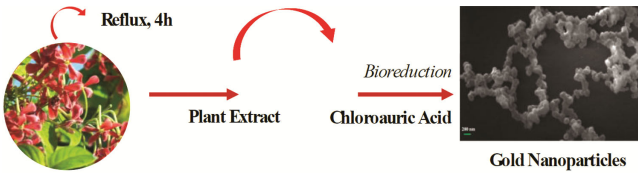

Fig. 1 — Graphical flowchart of the synthesis process

excitation of electrons from occupied *d* bands into states above the Fermi level. Following electron–phonon and hole–phonon scattering process results in energy loss and ultimately photoluminescent recombination of an electron from an occupied *sp* band with the hole. The PL spectra of Au nanoparticles generated by the bio-reduction of chloroauric acid by aqueous petal extract of *C. indicum* are shown in Fig. 3. All of the AuNPs produced were found to be luminescent, emitting at 530-555nm for an excitation of 450 nm. The PL spectrum demonstrates that when aqueous ammonia is added, the AuNPs exhibit a substantial red shift and reduction in intensity.

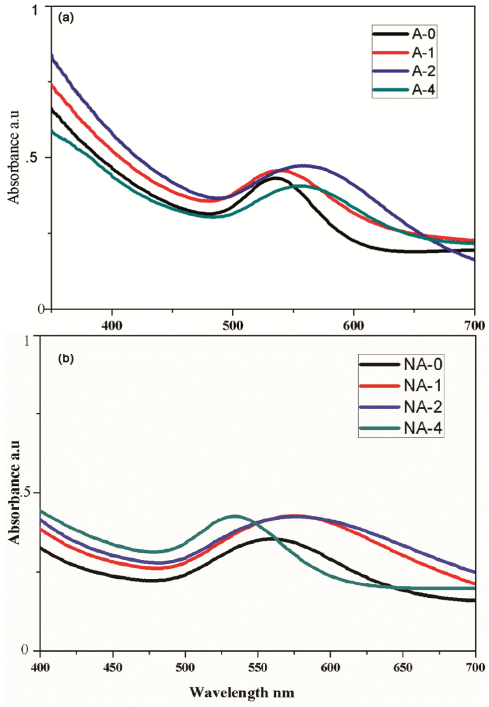

Fig. 2 — (a) UV-vis spectroscopy of gold nanoparticles synthesized at different stirring time using aqueous ammonia and (b) UV-vis spectroscopy of gold nanoparticles synthesized at different stirring time without aqueous ammonia

Scanning Electron Microscopy (SEM)

Figure 4 shows SEM micrographs of gold nanoparticles obtained at different stirring durations with aqueous ammonia. The reduction of gold ions with a plant extract in the presence of aqueous ammonia results in a variety of nanostructures (spherical, cubical etc.). At zero-hour, particle conglomeration was seen. Increased stirring duration from zero to two hours results in the creation of well-

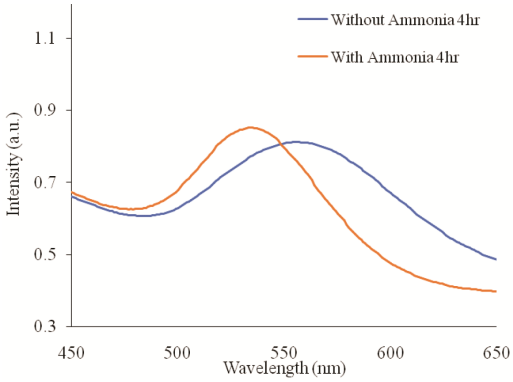

Fig. 3 — PL spectrum of AuNPs with and without addition of aqueous ammonia

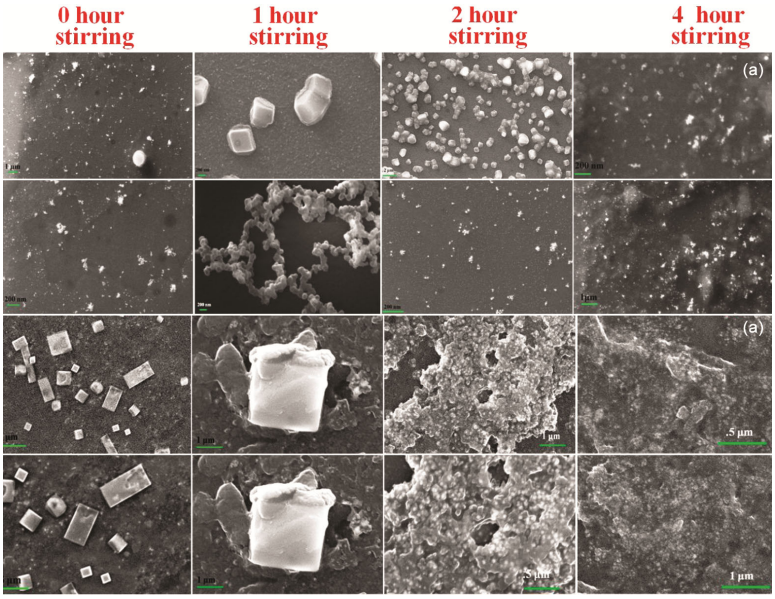

Fig. 4 — (a) SEM micrographs of gold nanoparticles synthesized at different stirring time using plant extract and aqueous ammonia and (b) SEM micrographs of gold nanoparticles synthesized at different stirring time using only plant extract.

dispersed and compact nanocubes. After 2 h of stirring, nanoparticles with fine granules are seen; whereas, at four hours of stirring, heavily agglomerated AuNPs can be observed, implying that AuNPs have a low stability at 4 h of stirring.

The SEM microstructures of gold nanostructures utilising only plant extract and no ammonia are shown in Figure 4b. AuNPs with cubical and rectangular shapes have developed in this instance. Agglomeration occurs as a result of the solution being stirred for 0, 1 and 2 h, respectively, and non-uniform structures may be seen quite clearly in SEM images. As a result, we can conclude that the presence of aqueous ammonia improved the formation and stability of AuNPs, but rather put another way, that ammonia solution functions as a capping agent during AuNP synthesis.

Dynamic Light Scattering (DLS)

The DLS technique, also known as QELS (quasi-elastic light scattering), uses dynamic light scattering to determine the average particle size and radius distributions of nanoparticles. This is a Doppler effect-based phenomenon that incorporates Brownian motions of the particles within the substance. These oscillations in scattering intensity are time-dependent[19].

Dynamic light scattering (DLS) analysis was performed to evaluate the size distribution profile of the nanoparticles in suspension. In the absence of ammonia, the average diameters of synthesised gold nanoparticles were 41.41 nm, 48.37 nm, and 79.40 nm for 0, 1 and 2 hours of stirring, respectively, whereas the average size in the presence of ammonia was 11.856 nm, 45.14 nm, and 49.2 nm fr 0, 1 and 2 hours of stirring, respectively.

Figures 5a and 5b depict the radius distribution of the synthesised AuNPs. It demonstrates unambiguously that AuNPs synthesised in the presence of aqueous ammonia have a more uniform radius size distribution than NPs synthesised in the absence of ammonia. In both cases, AuNPs produced with 2 h stirring had a fine radius distribution, which is consistent with previous results.

Energy Dispersive X-Ray Spectroscopy

The elemental composition of AuNPs contained in the solution was determined using energy dispersive X-ray spectroscopy (EDX).The EDX plot in Figure 6a and 6b confirms the chemical composition of gold in terms of atomic percentage. Despite the presence of a gold signal, the presence of a silicon signal can be attributed to the thin coating formed on the glass substrate used for the EDX.

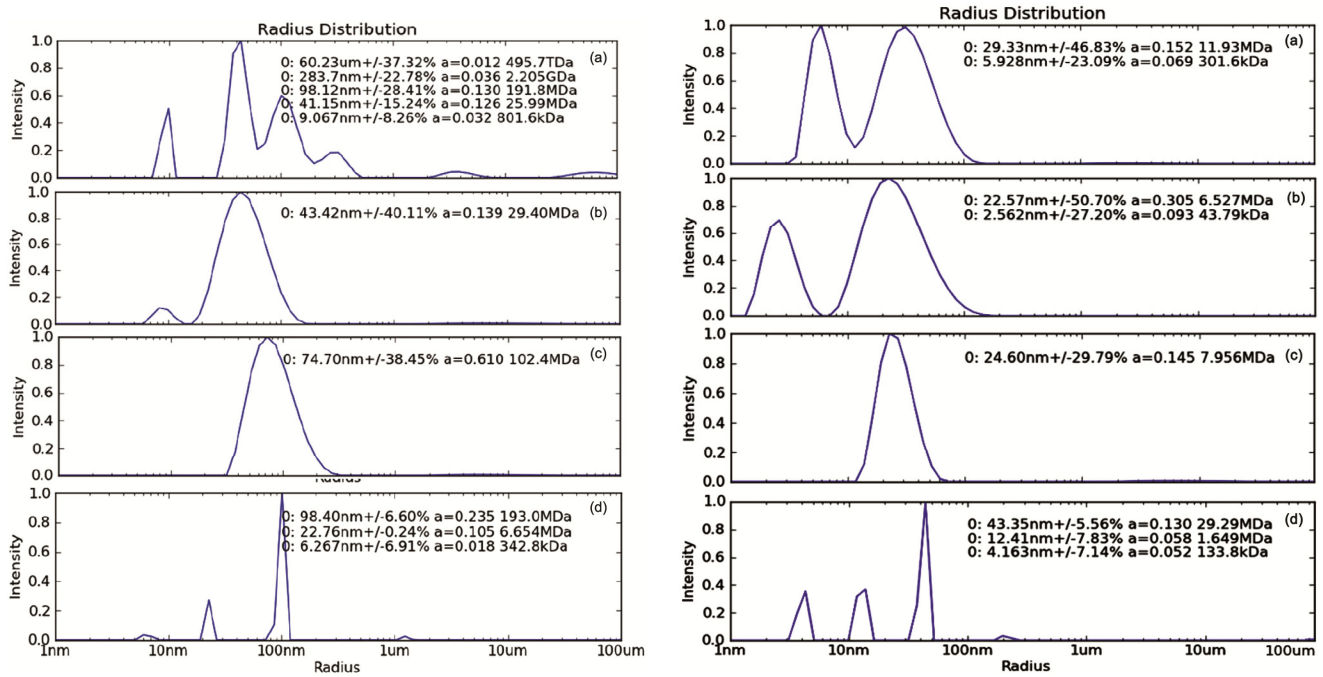

Fig. 5 — (a) DLS showing the radius distribution of the gold *nanoparticles* formed without ammonia (a – 0 h stirring, b – 1 h stirring, c – 2 h stirring and d – 4 h stirring) and (b*)* DLS showing the radius distribution of the gold *nanoparticles* formed with ammonia (a – 0 h stirring, b – 1 h stirring, c – 2 h stirring and d – 4 h stirring)

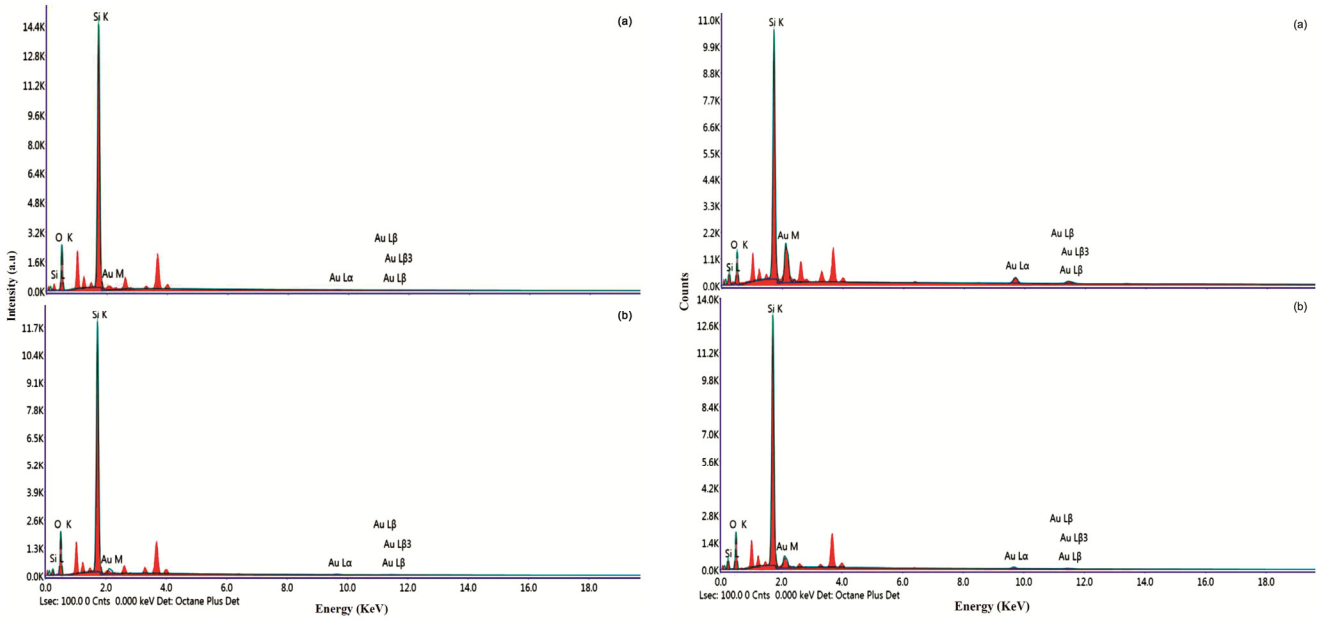

Fig. 6 — (a) EDX image of gold nanoparticles formed without ammonia a) 1-hour b) 2-hours stirring and (b) EDX image of gold nanoparticles formed with ammonia a) 1-hour b) 2-hours stirring

Conclusion

AuNPs of different sizes and shapes have been synthesised using aqueous plant extract of *Combretum indicum* as reducing agent. The SEM micrographs show that uniform cubical and rectangular nanoparticles are formed when ammonia is not present. As the stirring progressed, the aggregation of nanoparticles resulted in ambiguous/non-uniform morphology. The average size of the AuNPs was tuned by essentially altering the reaction time, as evidenced by the DLS data. In the absence of ammonia, the average diameters of synthesised gold nanoparticles were 41.41 nm, 48.37 nm, and 79.40 nm for 0, 1 and 2 hours, respectively, whereas the average size in the presence of ammonia was 11.856 nm, 45.14 nm, and 49.2 nm for 0, 1 and 2 hours of stirring, respectively. In comparison to NPs synthesized without ammonia, AuNPs generated with aqueous ammonia had a more consistent radius size distribution. In the both cases, AuNPs synthesized at 2-hour stirring exhibit fine radius distribution. UV Vis- spectra of the synthesised nanoparticles were used to determine the SPR. The SPR band of gold occurs initially at 550nm and ranges to 580 nm. The plasmon bands of AuNPs broaden as a function of time with a broader tail in the longer wavelength regions. The synthetic methods developed using the naturally derived reagents can be used alternative approach for preparing AuNPs. This green synthesis of nanoparticles has numerous advantages such as, process scaling up, economic viability, safety, non-toxic to environment and many more

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