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Green synthesis of silver and gold nanoparticles using flower bud broth of *Couropita guinensis* Aublet

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Abstract: Metallic nanoparticles have remarkable attention due to their various size and shapes in the green synthesis protocol. We report the synthesis of silver and gold nanoparticles using *Couropita guinensis* flower bud broth as reducing agent in the present study. The UV- Visible (UV-Vis) spectroscopic analysis of silver and gold reaction media reveals that the Surface Plasmon Resonance (SPR) vibrations have absorption maxima at 410 and 535nm respectively. These absorption maxima values correspond to the formation of silver and gold nanoparticles. Fourier Transform Infrared (FT-IR) spectroscopic analysis explains that biomolecules present in the flower bud broth of *Couropita guinensis* become capping agents and are responsible in the synthesis and stabilization of silver and gold nanoparticles. X-ray diffraction (XRD) analysis shows the particle nature and size. Energy Dispersive X-Ray (EDX) analysis and Scanning Electron Microscopy (SEM) confirm the significant presence of elemental silver and gold nanoparticles in respective reaction media. The obtained silver nanoparticles were almost spherical in shape. The gold reaction medium shows anisotropic gold nanoparticles in a polydispersed manner.
Key words : *Couropita guinensis*, flower bud broth, gold nanoparticles, silver nanoparticles, polydispersed.

Introduction

The method of extra-cellular synthesis of metal nanoparticles gained quick attention among researchers due to its rapid reduction process, cost effectiveness, simplicity in protocol, non toxicity and eco friendliness. Certain biomolecules present in the plant extract reduce the monovalent silver ion to uncharged atoms and these atoms aggregate to reach nano-size, other biomolecules of the plant extract envelope or 'cap' them to prevent their further aggregation[1]. The bioreduction behaviour of plant extracts produces polydispersed nanoparticles with different size and shapes on exposure to metal compounds. Recently much attention has been focussed towards controlling the shape and size of metal nanostructures as all the magnetic, catalytic, electrical and optical properties of metal nanostructures are influenced by their shape and size[2]. Nanoparticles have wide range of applications in the field of biology, medicine, electronics, food industry, environmental applications and cosmetics[2,3,4].

Nowadays several researchers are employed in the phytomediated synthesis of various metal nanoparticles such as silver, gold, palladium, copper and selenium due to their wide range of applications in various fields. Among them silver nanoparticles are very potential because of their unique physical, chemical and optical properties. They exhibit high antimicrobial activity against various pathogenic organisms[5] and the antitumor activity against various cancerous cell lines[6]. Silver nanoparticles are also used as diagnostic applicative biological tags and biosensors and antibacterial agents in apparel, cosmetics, footwear, wound dressings, paints, and plastics, in addition to thermal, electrical, and optical applications[7]. Gold nanoparticles are widely used in biomedicine such as tissue, tumour engineering, drug delivery and delivery of DNA vaccine using gene gun gold nanoparticles[8,9,10]. The present study is therefore aimed to synthesize silver and gold nanoparticles in an eco-friendly manner using the flower bud broth of *Couropita guinensis* and characterize them with various techniques such as UV-Vis spectroscopy, FTIR, XRD, SEM and EDX analyses.

Experimental Design

The silver nitrate ($AgNO_3$ 99.0%) and Gold (III) chloride trihydrate ($HAuCl_4$ 3H2O, 99.0%) were purchased from Himedia Laboratories Pvt Ltd (Mumbai, India). The flower buds of *Courpita guianensis* Aublet (Family: *Lecythidaceae*). were collected from the campus of Ayya Nadar Janaki Ammal College, Sivakasi, Tamilnadu, India. It is a tree of up to 30-35 metre tall with brown coloured bark and hard woody in texture. With obovate leaves appeared as clusters at the end of branches with entire margins and acute apex. Flowers are derived from the trunk of the tree as cauline inflorescence (Fig.1). Flowering usually occurs in two different seasons depending on the climatic conditions.

Fig. 1 Flower bud of *Couropita guinensis*

The collected flower buds were thoroughly washed with tap water followed by distilled water to remove the surface contaminants and partially dried for 24 hours under the shade. The partially dried flower buds were ground to make a paste using motor and pestle without adding any solvent. 10g of the flower bud paste was added to 100ml of distilled water and boiled at 70-80° C for ten minutes to prepare the flower bud broth[11,12]. 10ml freshly prepared flower bud broth was quickly resuspended in 90ml of an aqueous solution of silver nitrate. 10ml freshly prepared flower bud broth was quickly added in 90ml of an aqueous solution of gold chloride for the bioreduction of gold ions in to gold nanoparticles, [13,14].

These suspensions were kept in an incubator cum shaker (Orbitek-Model) with 150 rpm at 36°C for 24 hours. From each of this reaction media a small aliquot of the sample was taken after the centrifugation and used to characterize the silver and gold nanoparticles, that were synthesized in their respective reaction media. The characterization was performed through the following analyses: UV-Vis, FT-IR, XRD, SEM, EDX and TEM.

Results and Discussion

The colourless solution of silver nitrate (90ml) was mixed with pale brown coloured flower bud broth of *Couropita guinensis* (10ml) changed its colour to pale yellow at initial hours of incubation and started to

became pale brown at 3h of incubation (photograph not shown). The intensity of the colour was stable for a prolonged period *ie*., more than sixty days from the incubation period. The colour change indicates the formation of silver nanoparticles in the reaction medium of *Couropita guinensis*. However, the addition of pale yellow coloured gold chloride solution and pale brown coloured flower bud broth turned the reaction medium of *Couropita guinensis* in to ruby red colour at zero hour of reaction. This ruby red colour remains as such for a while and starts to became dark at one hour of incubation and thereafter it becomes dark ruby red colour (Photograph not shown).

The prepared reaction media were monitored under UV-Vis spectrophotometer and the wavelength ranging from 350 to 700nm. The λ max of SPR band at 410 nm and the absorbance was raised up to 1.38 a.u.(Fig. 2). Time course of silver nanoparticles formation obtained with 1mM aqueous solution of silver nitrate and flower bud broth of *Couropita guinensis* explains that the maximum synthesis of silver nanoparticles is completed within three hours of the reaction. In this reaction medium 90 percent reduction completed in the first six hours and 10 percent reduction completed in the subsequent hours (Fig. 3).

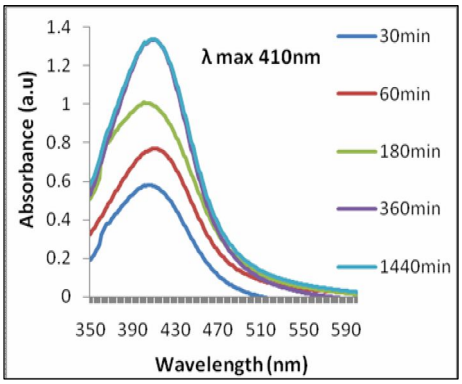

Fig. 2 UV-Vis spectrum of silver reaction medium at various time intervals

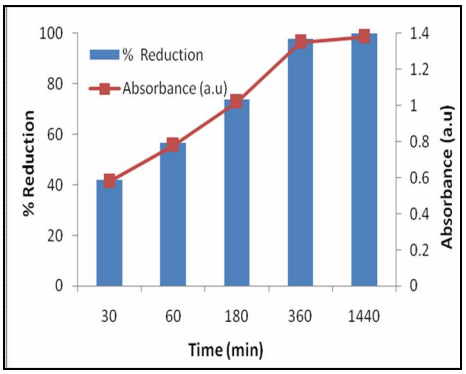

Fig. 3 Spectral plot of absorbance at 410nm (λ max) of SPR bands shown by silver reaction medium as a function of time

The gold nanoparticles gave an SPR band with λ max 535nm and the absorbance was raised up to 0.87a.u. (Fig.4). In the case of gold reaction medium, 82 percent reduction completed in the first six hours of incubation and remaining 18 percent reduction occurred in the subsequent hours (Fig.5). The rate of reduction in silver reaction medium is faster than gold reaction medium. Gold reaction medium shows a gradual and steady reduction process while comparing silver reaction medium, where the reduction is faster in the early hours. This differential response in the time course of reduction in each reaction medium may be due to the differential behaviour of biomolecules present in the flower bud broth as reducing agents.

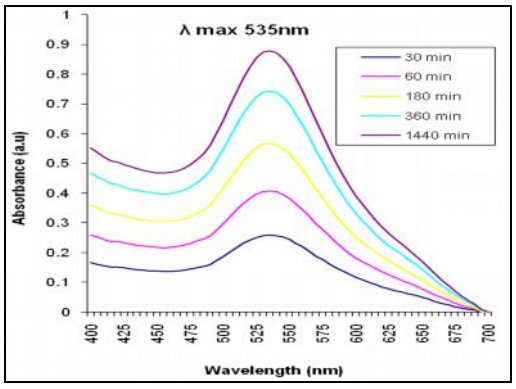

Fig. 4 UV-Vis spectrum of gold reaction medium at various time intervals

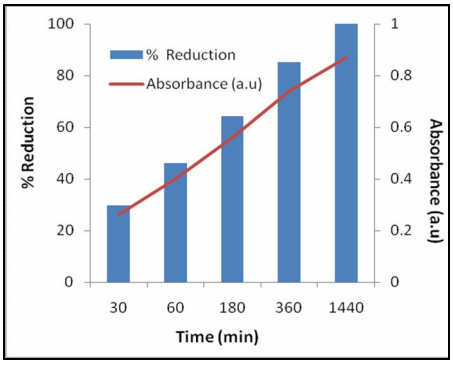

Fig. 5 Spectral plot of absorbance at 535nm (λ max) of SPR bands shown by gold reaction medium as a function of time

Both the SPR bands (Fig. 2 and 4) with single absorption maximum (λ max) obtained were very sharp and narrow. This correlates that the synthesized silver and gold nanoparticles are polydispersed in the reaction media with spherical in morphology[15,16,17,18,19].

FTIR spectroscopic analysis of metal nanoparticles were carried out to identify the possible biomolecules responsible for the reduction and stabilization of each reaction media with silver and gold ions into respective nanoparticles. The FTIR analysis of reaction medium with silver nanoparticles show peaks centered at 1670, 1452, 1393, 1338, 1193, 1112cm^{-1} while in gold reaction medium show peaks centered at 1670, 1521, 1456, 1400, 1336, 1191, 1122 cm^{-1} (Fig.6 and 7).

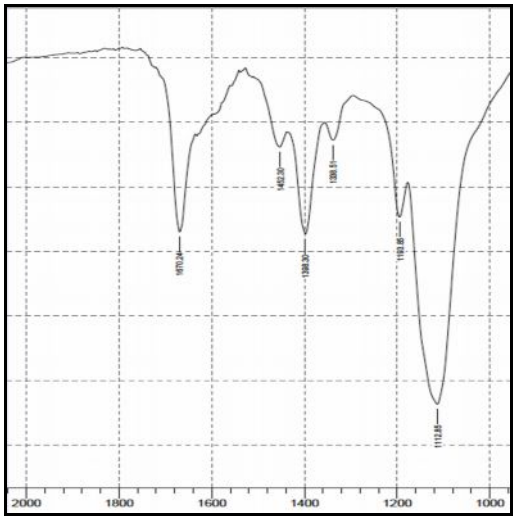

Fig. 6 FTIR spectrum of silver nanoparticles synthesized using flower bud broth of Couropita guinesis

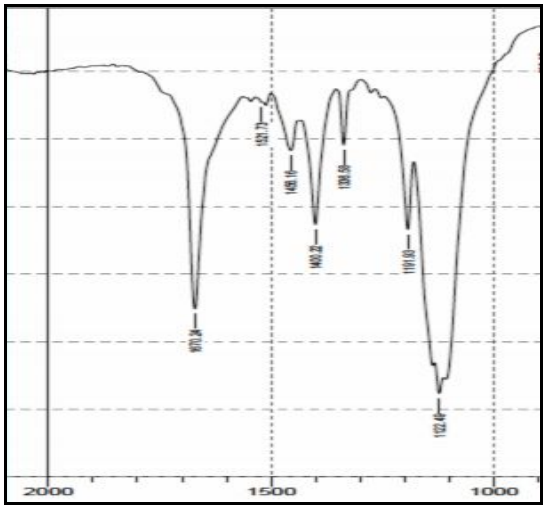

Fig. 7 FTIR spectrum of gold nanoparticles synthesized using flower bud broth of Couropita guinesis

The absorption peak located at 1670 cm^{-1} can be attributed to the stretching vibrations of C=O, NH2[20,21,22,14]. The absorption at 1400, 1452 and 1456 cm^{-1} is possibly due to the bending tendency of symmetric CH_3 groups within the acetyl and pyruvyl groups as substituents[23,24] and germinal methyl function respectively[24]. Peaks around 1191, 1193and 1122cm^{-1} may be due to the C-N stretching vibrations of aliphatic phenols, peaks around 1336 and 1338 cm^{-1} are due to N=O symmetry stretching typical of the nitro compound[25] and 1521 cm^{-1} for silver and gold reaction media may be due to amide I, arising due to carbonyl stretch in proteins[26] respectively may lead to the reduction and stabilization of silver and gold nanoparticles respectively.

Crystalline nature of metallic silver and gold nanoparticles were examined by X-ray diffractometer (Shimadzu XRD 6000)). Figs. 8 and 9 show the X-ray diffraction spectra of representative silver and gold nanoparticles. Many Bragg's reflections are visible in the XRD spectra of silver which are corresponding to the 2θ = 38^0 (111), 46^0 (200), in a lattice plane[27,28] and gold which are corresponding to the 2θ =38^0(111), 44^0(200), 64^0(220) and 77^0 (311) [29] .

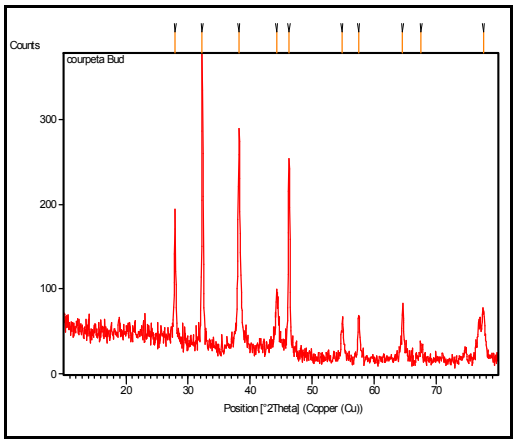

Fig. 8 XRD spectrum of silver nanoparticles synthesized using flower bud broth of Couropita guinesis

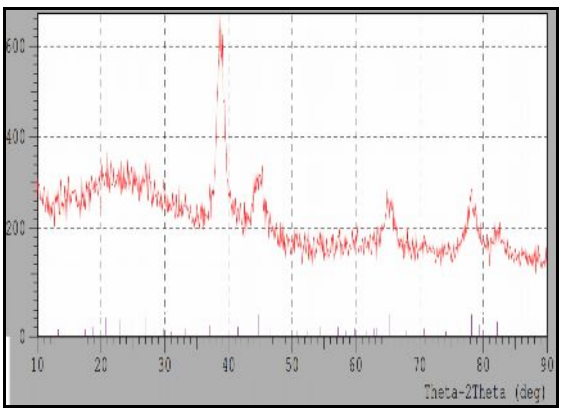

Fig.9 XRD spectrum of gold nanoparticles synthesized using flower bud broth of Couropita guinesis

On the basis of these Bragg's reflections, we confirmed that the synthesized silver and gold nanoparticles are Face Centered Cubic (FCC) and crystalline in nature respectively[30,31]. The figs. 10 and 11 showed the SEM images of silver and gold nanoparticles respectively that are synthesized in the present study. The obtained silver nanoparticles are seen almost spherical and closely arranged where as the gold nanoparticles are various shapes and loosly arranged.

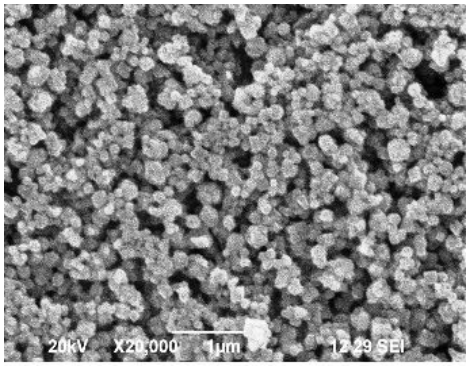

Fig. 10 SEM image of silver nanoparticles synthesized using flower bud broth of Couropita guinensis

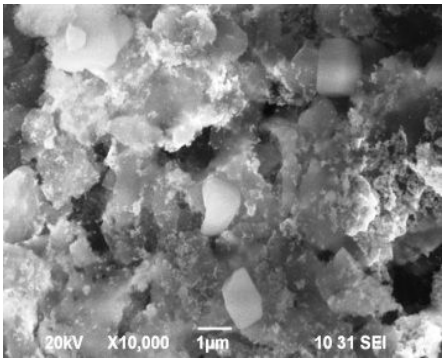

Fig.11 SEM image of gold nanoparticles synthesized using flower bud broth of Couropita guinensis

The strong silver and gold peaks in the EDX- spectra (Figs. 12 and 13) confirm the significant presence of elemental silver and gold.

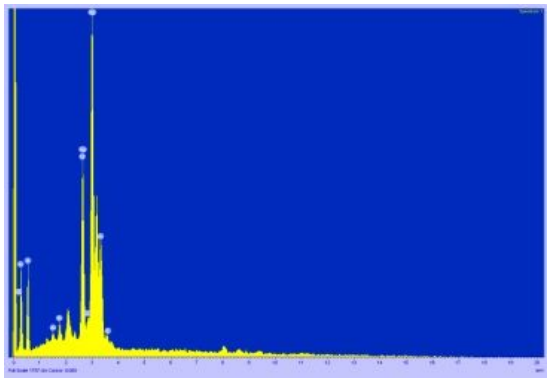

Fig. 14 EDX pattern of silver nanoparticles synthesized using flower bud broth of *Couropita guinensis*

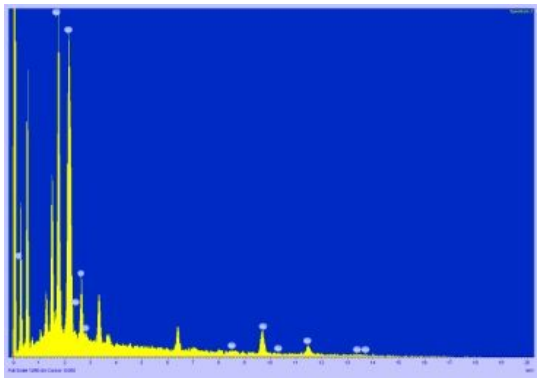

Fig.15 EDX pattern of gold nanoparticles synthesized using flower bud broth of *Couropita guinensis*

The metallic silver nanoparticles generally show typical optical absorption peaks approximately at 3KV due to Surface Plasmon Resonance[32,27]. The EDX peak of Ag along with Cl, and O as the mixed components present in the reaction medium. The strong elemental signal along with weak signals that may be originated from the biomolecules bound on the surface of the nanoparticles[33,11,27].

Conclusion

The present study shows the potentiality of flower bud broth of *Couropita guinensis* in the synthesis of silver and gold nanoparticles with different size and shape. The biologically synthesized silver and gold nanoparticles were stable at room temperature with size <50nm. Thus the present protocol of biological synthesis of silver and gold nanoparticles becomes green route and an alternative to physical and chemical methods as it is not involved of either toxic chemicals or toxic procedure.

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