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Sonochemical Synthesis of Gold Nanoparticles by Using *Piper betle* Leaf Broth as a Reducing and Capping Agent

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ABSTRACT

The use of biomolecules hosted products for synthesis of nano sized materials is of increasing interest to benign medical field. We report a biomolecule hosting, environmentally benign, sonochemical synthesis of gold nanoparticles by using Piper betle leaf broth as a reducing and capping agent. The aqueous reaction of medium containing gold nanoparticles showed a peak at 540 nm, studied by UV-Vis spectra. In addition, we determined the size of the nanoparticles and optical energy gap from the surface plasmon absorption peak. The crystalline structural characteristics of a biomolecule hosted gold nanoparticles were studied by X- ray diffraction. The morphology of nanoparticles was analyzed by scanning electron microscopy. The chemical composition of elemental presence in the medium was determined by energy dispersive spectrum. The presences of biomolecules which act as capping agents around the nanoparticles were studied by Fourier transform infrared spectroscopy.

Keywords: *Sonochemical synthesis, UV-Vis spectra, XRD, FTIR.*

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1. INTRODUCTION

Proliferation of green chemical nanoscience research has opened up novel fundamental and frontiers in material science and medical research. Integration of green chemistry principles to nano is one of the key issues of nanoscience and technology research. Interdisciplinary nanoscience research involving physicists, chemists, biologists and material engineers are concerned about the need for developing eco-friendly methods to synthesize of nano materials [1, 2]. Among the noble metal nanoparticles, gold nanoparticles has fascinating chemical and physical properties and has important value in the fundamental and application research fields [3, 4]. Traditionally, nanoparticles have been prepared by a number of physical and chemical methods like laser ablation, pyrolysis, lithography, chemical vapor deposition, sol-gel technique and electro deposition techniques, which are slow, expensive and often involve the use of toxic, hazardous chemicals which may pose environmental risks and human health [5]. Among these synthesis methods, the use of ultrasound offers the sonochemical reduction drew particular attention due to the generation of nanoparticles with smaller size [6]. Nature provides a clue in the form of biomolecules that can be effectively utilized in capping nanoparticles. For instance, a great deal of effort has been put into the green synthesis of inorganic materials, especially, metal nanoparticles [7]. Consequently, there have been interesting reports on the preparation of metal nanoparticles employing biomimetic entities such as enzymes, bacteria, viruses, fungi, yeast and plant or plant leaf extracts [8–13]. Green chemistry is reducing or eliminating the generation of substance hazardous to human health. The environment strategies of addressing the mounting environmental concerns with current approaches include the use of environmentally benign solvents, biodegradable polymers and non-toxic chemical [14]. The *Piper betle* is a traditional medicinal plant of India, which is a source of diosgenin, triterpenes, alkaloids, nitrosoguvacoline, propenylphenols and piperbetol [15]. *Piper betle* leaves have long been studied for their diverse pharmalogical actions such as anti-inflammatory, anti-oxidant, radio protective, anti-fungal, anti-bacterial and anti-allergic activities [16]. So far, there have been no reports on the synthesis of nanoparticles from *Piper betle* leaf extract by using sonochemical synthesis. In this paper, we report on the sonochemical synthesis of gold nanoparticles using *Piper betle* leaf extract as a reducing agent and stabilizer.

2. EXPERIMENTAL

2.1. Materials

Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4$. $3H_2O$) was obtained from Sigma Aldrich (USA). The fresh *Piper betle* leaves were collected from the retail shop near by the Sri Venkateswara University campus, Tirupati, Andhra Pradesh, India. The solutions were prepared with nanopure water which was obtained by passing twice distilled water through a milli-Q system.

2.2. Preparation of Piper betle Leaf Broth

The fresh *Piper betle* leaf extract used for the reduction of gold ions was prepared by taking 20 gm of thoroughly washed, finely cut leaves in 500 ml Erlenmeyer flask along with 100ml of deionized water and then boiling the mixture for 2 min before decanting it. Further, the extract was filtered with Whatman No. 1 filter paper and stored at 4°C and used for further experiments.

2.3. Sonochemical Synthesis of Gold Nanoparticles

In a typical experiment, 0.5 ml of the leaf extract was added to 10 ml of 1mM $HAuCl_4$ aqueous solution. Synthesis of gold nanoparticles was prepared by sonication of the solution by a high power ultrasonicator (POWER SONIC 300). The bioreduced gold solution (0.5 ml) was used to measure UV-Vis spectra. The particle suspension was diluted in the order 1:10 ratio with nanopure water, to avoid the errors that could occur due to the high optical density of the solution.

3. RESULTS AND DISCUSSION

3.1. UV-Visible Absorption Spectroscopy

The UV-Visible absorption spectroscopy is a valuable tool for understanding the kinetics coagulation of chloroaurate ions. The bioreduced aqueous solution was examined under ultrasound during its reaction with leaf extract. The colour of the gold solution gradually turned from yellow to pink. Subsequently, we observed that with time further, the colour changed from pink to deep red. Under ultrasound, the progress of reaction between the *Piper betle* leaf broth and the aqueous chloroauric acid as a function of time was recorded on spectrophotometer (PERKIN-ELMER LAMBDA 25) at room temperature is shown in Figure 1. With increasing time, the full width half maximum decreases which is supporting the reduction of size of the particle. Strong absorption band was observed at 540 nm supporting the formation of spherical gold nanoparticles in solution. In recent years, the gold nanoparticles prepared by eco-friendly procedure have widely applied in medicinal fields. The calculation of size of the particle is important, because the small-sized nanoparticles are capable of penetrating across the membrane easily [17]. The calculation of size of particles by electron microscoptic techniques is good, but it is not simple and fast. The calculation of nanoparticles size with kinetics of reaction is not reliable. A simple, fast spectroscopic method is used to calculate size of the nanoparticles. The average radii of the gold nanoparticles can be estimated by the equation $R=V_f/\Delta\omega_{1/2}$ [18], where V_f is the Fermi velocity of the electrons in the metal. $\Delta\omega_{1/2}= 2\Pi C\ (\Delta\lambda/\lambda^2_p)$, where $\Delta\lambda$ is full width half maximum wavelength and λ_p is plasmon peak wavelength. The average size of the gold nanoparticles was found to be 6.5 nm.

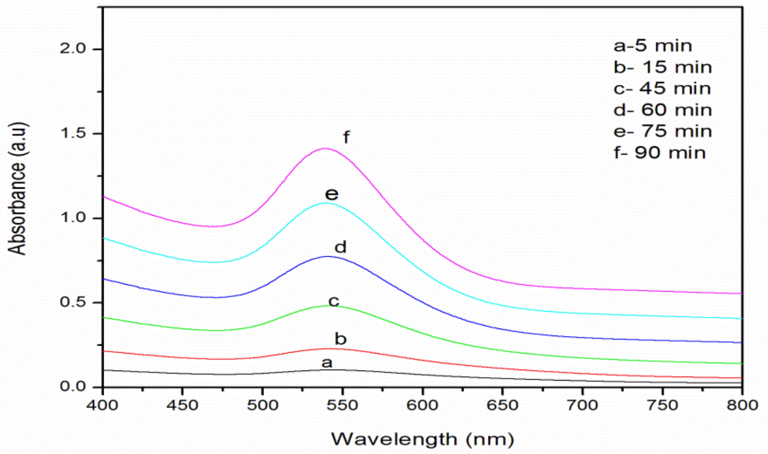

Fig. 1: *UV-Vis Spectra of Gold Nanoparticles at Different Time Intervals.*

3.2. Calculation of Optical Band Gap

The solid state materials illustrated with optical band gap is an important parameter. The band gap of material is defined as the gap between the valance and conduction bands. There are two kinds of optical transitions at the fundamental absorption edge, direct and indirect transitions both of which involve the interaction of an electromagnetic wave with an electron in the valence band. The group energy levels are quite different between nanomaterials and bulk materials, in that the nanomaterials have larger band gaps and consist of more discrete energy levels. This observation may be attributed to the various quantum confinement effects within nanoparticles. We calculated the optical band gap energy for gold nanostructures from the UV-Vis absorption spectrum. The relation between optical absorption coefficient α and hν is expressed as $(\alpha h\nu)^2 = C\,(h\nu - E_g)$ where C is a constant. Figure 2 shows the plot of $(\alpha h\nu)^2$ versus hν for the gold nanostructures synthesized from the *Piper betle* leaf broth. The energy gap is estimated from the extrapolated linear portion of the plot. In the present case, the energy gap is found to be 2.0 eV and it is in good agreement with the reported values in the literature [19].

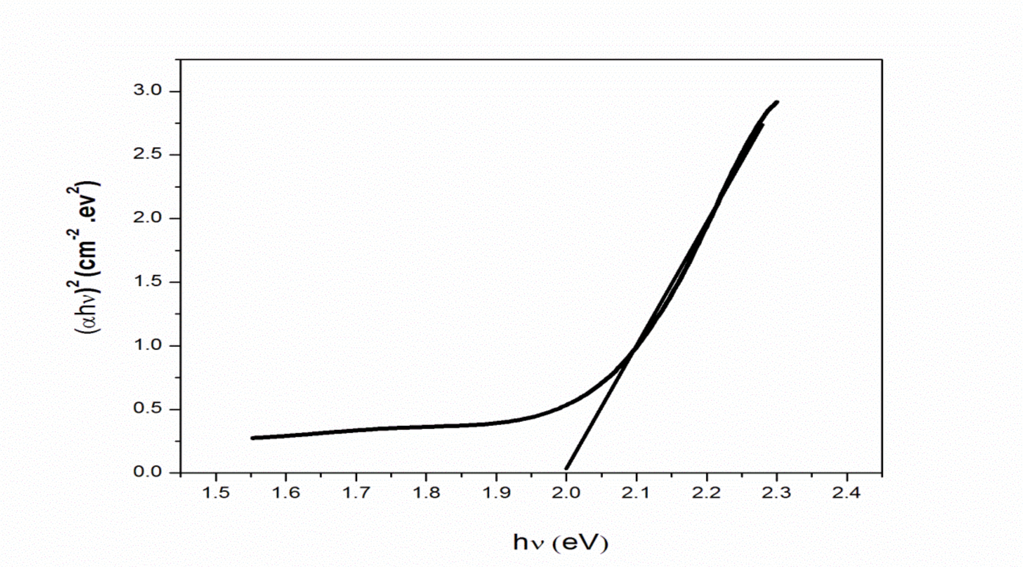

Fig. 2: *Plot of $(\alpha h\nu)^2$ Versus Photon Energy (hν) of Gold Nanoparticles*.

3. 3. Crystalline Structural Analysis of Gold Nanoparticles

An X-ray diffraction (XRD) measurement was done of a thin film of the synthesized gold solution was drop coated onto a glass slide and an INEL X-ray diffractometer. The diffraction pattern was recorded by Co-kα_1 radiation with λ of 1.78A° in the region of 2θ from 20º to 90º at 0.02º/ min. and the time constant was 2 sec. The size of the nanoparticles was calculated through the Scherrer's equation. The crystalline nature of gold nanoparticles was studied with the aid of an X-ray diffraction as shown in Figure 3. The number of strong Bragg's diffracted peaks was observed at 44.6º, 52.1º, 76.8º and 93.4º corresponding to the (111), (200), (220) and (311) facets of the face centered cubic lattice of gold were obtained. The average domain size of the gold nanoparticles was found to be 3.2 nm, and it was done by using the width of the (111) Bragg's reflection, which was in consonance with the size of the particle calculated from UV-Vis analysis.

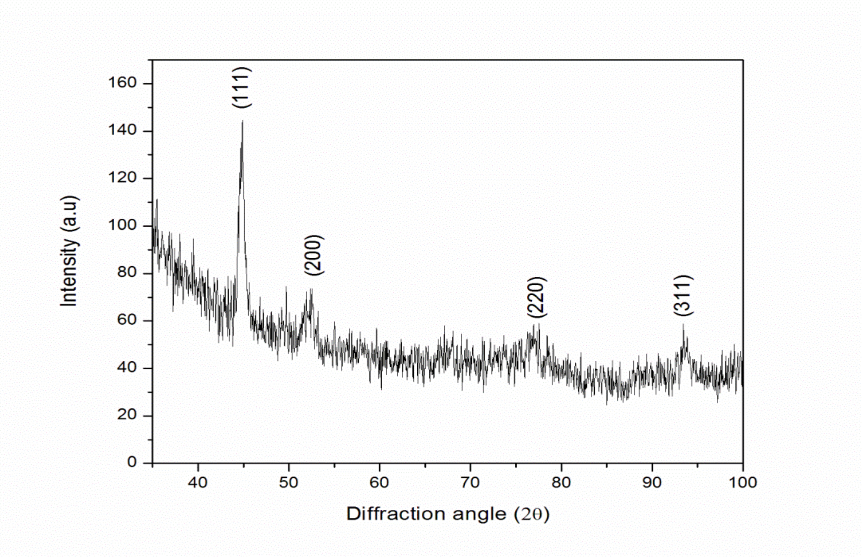

Fig. 3: *X-Ray Diffraction Spectrum of Gold Nanoparticles.*

3.4. Scanning Electron Microscopy Studies

The morphology of the nanoparticles was studied with scanning electron microscopy. The SEM samples of the aqueous suspension of gold nanoparticles were prepared by dropping the suspension onto clean glass plate and allowing water to completely evaporate. SEM observations were carried out on a PHILLIPS FEI TECNAI G2S TWIN instrument. The SEM image shows that the gold nanoparticles are predominantly spherical in shape as shown in Figure 4.

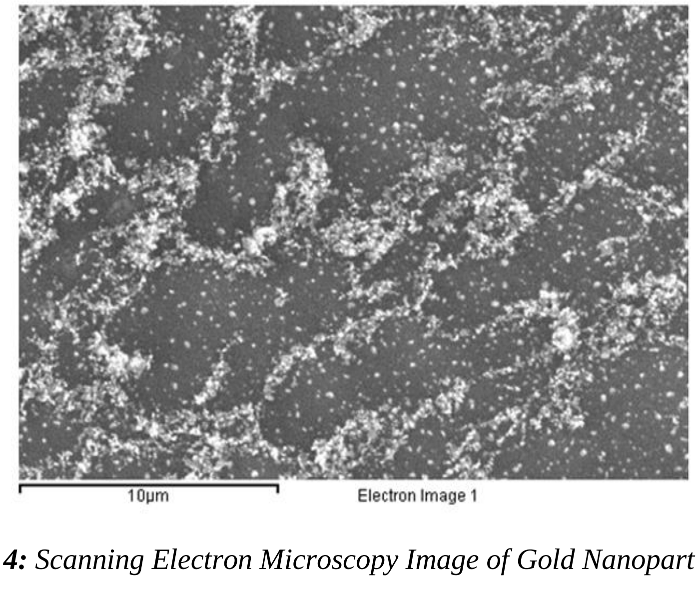

Fig. 4: *Scanning Electron Microscopy Image of Gold Nanoparticles.*

3.5. Energy Dispersive X-ray Measurements

The energy dispersive X-ray analysis (EDS) reveals the stoichiometric elemental chemical composition in fabricated nanoparticles. The EDS revealed the formation of a strong signal in the gold region and confirmed the formation of gold nanoparticles as shown in Figure 5.

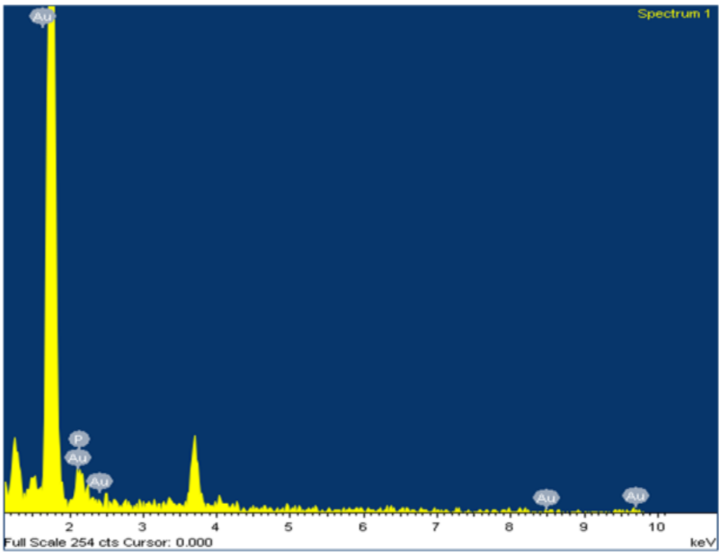

Fig. 5: *Energy Dispersive X-ray Spectrum of Gold Nanoparticles.*

3.6. Fourier Transform Infra-red Spectroscopy

FTIR has emerged as a valuable tool for understanding the involvement of surface functional biological groups in metal interactions. For fourier transformed infrared (FTIR) measurements, the bioreduced aurate ions aqueous component was centrifuged at 15,000 rpm for 20 min. The dried sample was grinded with KBr pellets and analyzed on THERMO-NICOLET IR200 FT-IR spectrometer which was operated at a resolution 4 cm^{-1} in the region of 4000–400 cm^{-1}. Figure 6 shows the FTIR spectrum of synthesized gold nanoparticles reduced by *Piper betle* leaf broth. It confirmed the fact that the identified biomolecules act as the reducing and efficient stabilizing agents of the gold nanoparticles. The band 3427 cm^{-1} is due to O–H stretching as also the H– boned alcohols and phenols. The peak at 2920 cm^{-1} corresponds to aldehydic C–H stretching. The band at 2359 cm^{-1} indicates the C≡N stretch nitriles. The peak at 1620 cm^{-1} represents to the vibrational modes of C=C double bonds of these molecules. The 1549 cm^{-1} can be assigned to the N–H bend secondary amines. The band at 1365 cm^{-1} indicates the N=O bend nitro groups and 1060 cm^{-1} corresponds to the vibrational modes of esters and ethers. From the FTIR spectrum, it may be confirmed that phenolic compounds was probable capping agent on the nanoparticles [20]. When the metal nanoparticles are in the form of solution, they must be stabilized against the vander waals forces of attraction which may otherwise cause coagulation. It is known that *Piper betle* leaf broth is source of tannins, alkaloids, triperpens and phenolic compounds. To understand the trends of phenolic compounds in enabling nanoparticles nucleation, phenolic compounds have –OH groups in its structures and it has O–dihydroxylphenyl groups which are capable of taking part in redox reactions to form quinones. Phenolic compounds can be used as both reducing and stabilizing agents and it is difficult to distinguish between the reducing and stabilizing roles of the phenolic compounds. In this procedure, for the production of gold nanoparticles using leaf extract, ultrasound is used for formation of nanoparticles within few minutes.

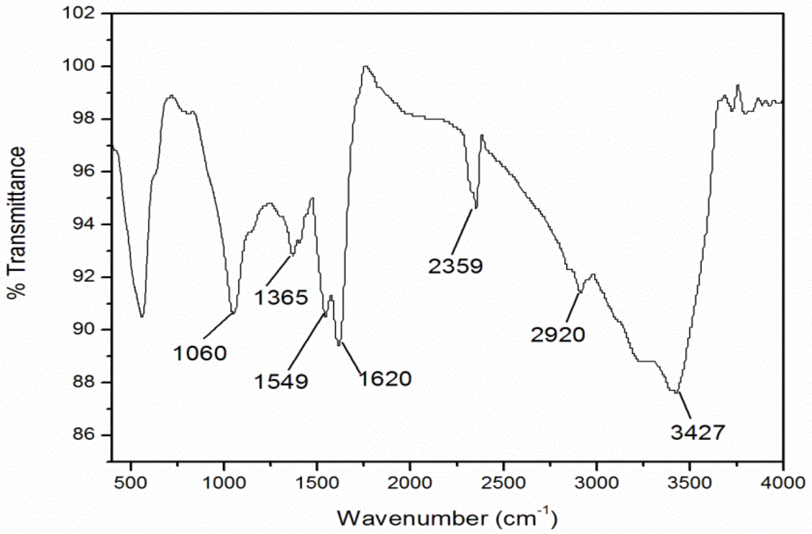

Fig. 6: *FTIR Spectrum of Phytofabricated Gold Nanoparticles.*

4. CONCLUSIONS

The synthesis of spherical gold nanoparticles using leaf broth of *Piper betle* provides an environment friendly, simple, cost-effective and efficient route for the benign nanoparticles. In this synthesis, ultrasound is used for reducing the gold nanoparticles in few minutes. From the absorption maxima obtained by UV-visible spectrum, the theoretical particle size was calculated and it was compared with calculated particle size from the XRD studies. From a technological point of view, these obtained gold nanoparticles have many potential applications in the medicinal fields, catalysis, optoelectronics, modern nanobiotechnology, materials science and this novel procedure has several advantages such as the compatibility for medical and pharmaceutical applications, and large scale commercial productions as well.

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