Synthesis of Au-Ag Bimetallic Nanoparticles Using *Melastoma Malabathricum* Flower Extract

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Abstract: *Au-Ag bimetallic nanoparticles exhibit unique optical, electronic and catalytic properties different from their monometallic counterparts. This paper reports a simple cost-effective and eco-friendly solution based phytosynthesis of Au-Ag bimetallic nanoparticles. Synthesis of bimetallic Au-Ag nanoparticles was carried out using the co-reduction of mixture of different proportions of 0.25 mM* $AgNO_3$ *and 0.25 mM* $HAuCl_4.3H_2O$ *solutions at 50* ^oC *using Melastoma malabathricum flower extract. Synthesized nanoparticles were characterized using UV-Vis spectrophotometer, Field Emission Scanning Electron Microscope (FESEM) equipped with Energy Dispersive X-ray analysis (EDX) instrument and Transmission Electron Microscope (TEM). The presence of single surface plasmon resonance peak in the absorption spectra suggested the formation of alloy type Au-Ag nanoparticles. The morphology studies were carried out using micrographs taken using FESEM and TEM. TEM micrographs revealed the presence of both alloy type and core–shell type bimetallic Au-Ag nanoparticles. The elemental analysis carried out using EDX spectrum showed the presence of both Au and Ag in the synthesized bimetallic nanoparticles.*

Key Words: *Bimetallic Au-Ag Nanoparticles, Co-reduction, FESEM, TEM.*

1. Introduction

Desirable features of two or more noble metals like Au, Ag, Pt, Pd can be combined to form new functional materials exhibiting interesting physicochemical properties. The structure as well as size of bimetallic nanoparticles depends on the preparation conditions, kinetics of reduction of metal ions, miscibility of different metals and so on. As Au possesses relatively low reactivity, it easily alloys with other noble metals like Ag, Pd or Pt.

Among bimetallic nanoparticles, bimetallic Ag-Au nanoparticles have received considerable attention from several researchers as they possess size dependent optical, electrical, electronic and catalytic properties that are not exhibited by their monometallic nanoparticles [1-7]. Various synthesis techniques like chemical [1, 2], radiolytic [3], photolytic [4], laser assisted [5], laser ablation [6] etc. employing either co-reduction or simultaneous reduction have been reported to prepare Au-Ag nanoparticles of alloy type or of core-shell type decided by the homogeneous or heterogeneous mixing of atoms using respective metal precursor solutions. As per literature, co-reduction of two metal precursor solutions using reducing agents like sodium citrate, sodium borohydride etc. is best suited for the synthesis of alloy type bimetallic nanoparticles where as successive reduction is best suited for core-shell type wherein metal ions of one metal are reduced and deposited on the surface of preformed nanoparticles of other metal acting as core [2, 3, 6-8]. Synthesis of Au (core)-Ag (shell) bimetallic nanoparticles using extract prepared from neem leaf [9], mushroom [10], gripe water [11], persimmon leaf [12] etc. as reducing agent have been reported to name a few. The use of Au-Ag bimetallic nanoparticles as Surface Enhanced Raman Scattering (SERS) substrate [8, 11, 13, 14], cytochemical marker [15], catalysis [7] have been reported.

Owing to the difference in the reduction potentials of Ag and Au, Au^{3+} ions undergo quick reduction when compared to Ag^+ ions. Due to this reason, if both the Au and Ag precursor solutions are subjected to simultaneous reduction, Au should act as core as Au^{3+} ions undergo quick reduction and the reduced Ag atoms deposit on the AuNPs thus leading to Au (core)-Ag (shell) nanoparticles. However, the successive reduction method in which Ag is reduced on the preformed AuNPs also yields Au (core)-Ag (shell) nanoparticles. *Melastoma malabathricum* is a flowering plant commonly called as Malabar Melastome belongs to the family Melastomataceae. It is also known as Indian rhodendron or senduduk (called as nekkarika in vernacular) and is being used in traditional medicine [18]. Experiments performed with *Melastoma malabathricum* flower extract as reducing agent at room temperature with precursor solution of Au and Ag have shown the rapid reduction of Au precursor solution when compared to the slow reduction of Ag precursor solution [18, 19]. The reduction of Ag precursor solution was found to increase with the increase in temperature. The results of experiments carried out by performing simultaneous reduction of both Au^{3+} ions and Ag^{+} ions at 50 °C using *Melastoma malabathricum* flower extract is presented in this study.

2. Synthesis and Characterization of Au-Ag Bimetallic Nanoparticles

$HAuCl_4 \cdot 3H_2O$ purchased from CDH and $AgNO_3$ obtained from Sigma-Aldrich were used as received as the source of Au^{3+} ions and Ag^{+} ions respectively. Double distilled water was used to prepare all aqueous solutions. Fresh flowers of *Melastoma malabathricum* were collected from Rayee (Karnataka), India. 0.3 g of thoroughly washed fresh petals of *Melastoma malabathricum* were added to a beaker containing 25 mL of double distilled water and heated slightly (40 °C) followed by filtration after the violet coloured petals became colourless. The filtered extract was used to prepare bimetallic Au-Ag nanoparticles.

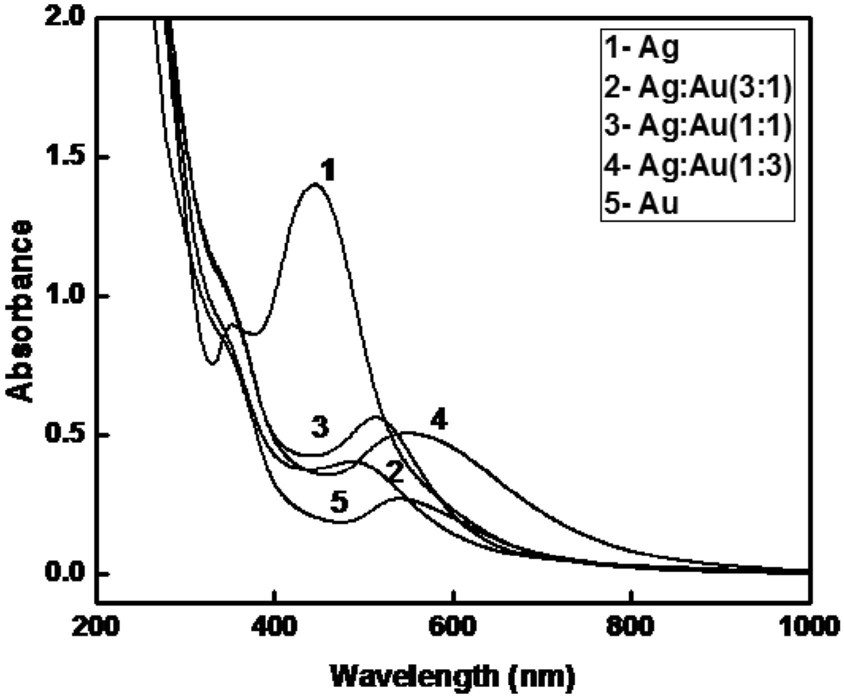
The co-reduction of the solution mixture containing both Au^{3+} ions and Ag^{+} ions was carried out at 50 °C using *Melastoma malabathricum* flower extract. Bimetallic Au-Ag sample named Ag:Au (3:1) was prepared by adding 4 mL of flower extract to the solution mixture containing 12 mL of 0.25 mM $AgNO_3$ and 4 mL of 0.25 mL of $HAuCl_4$. Sample Ag:Au (1:1) was prepared by adding 4 mL of flower extract to the solution mixture containing 8 mL of 0.25 mM $AgNO_3$ and 8 mL of 0.25 mL of $HAuCl_4$ and the sample Ag:Au (1:3) was prepared by adding 4 mL of flower extract to the solution mixture containing 4 mL of 0.25 mM $AgNO_3$ and 12 mL of 0.25 mL of $HAuCl_4$. All the 3 samples were prepared under continuous stirring conditions. For comparison purposes, separate Ag and Au nanoparticle samples (AgNPs and AuNPs) were also prepared by adding 4 mL of flower extract to 16 mL of 0.25 mM $AgNO_3$ and $HAuCl_4$ precursor solutions under same synthesis conditions. Shimadzu UV–1800 UV-Vis spectrophotometer was used to acquire the UV-Vis absorbance spectra for all the solutions. Micrographs were taken using Carl Zeiss Field Emission Scanning Electron Microscope (FESEM) model Σigma operated at an accelerating voltage of 5 kV fitted with an Energy Dispersive X-ray analysis (EDX) instrument (DST PURSE Laboratory, Mangalore University, Mangalagangotri) and Transmission Electron Microscope (TEM) model JEOL 3010 operated at 200 kV (TEM instrument at Sprint Testing Solutions, Nagpur). Samples were dried on a piece of thin aluminium sheet and dried on carbon coated copper grid for FESEM and TEM analysis respectively.

3. Results and Discussion

3.1 UV-Vis Studies

Metallic nanoparticles especially of Ag and Au exhibit an optical property known as Surface Plasmon Resonance (SPR). When an incident light is incident on metal surface, SPR occurs due to the collective oscillation of conduction band electrons which undergo resonance with the oscillating electric field of incident light. SPR depends not only on the size and shape of the nanoparticles but also on the dielectric medium in which the nanoparticle is present [6-10]. Normally, spherical AgNPs exhibit absorbance peak at about 400- 450 nm and spherical AuNPs exhibit absorbance peak at about 520- 550 nm. Two plasmon bands will appear in the wavelength range 400 – 550 nm for the physical mixture containing both AuNPs and AgNPs or for core shell Au-Ag nanoparticles [7, 16]. Typical Au-Ag alloy nanoparticles exhibit single absorption band with the position of SPR peak dependent on the composition of Ag and Au in the system [1]. The SPR peak of Au-Ag alloy nanoparticles will lie in between SPR peak of AgNPs and AuNPs and is shifted from Ag to Au with decreasing Ag:Au molar ratio [17]. Figure 1 represents the UV-Vis absorbance spectra of the 5 samples Ag, Ag:Au (3:1), Ag:Au (1:1), Ag:Au (1:3) and Au. SPR peaks of Au-Ag nanoparticles were found to be 489 nm for Ag:Au (3:1) sample (curve 2), 513 nm for Ag:Au (1:1) sample (curve 3), and 550 nm for Ag:Au (1:3) sample (curve 4), where as the SPR peak observed under the same experimental conditions was at 445 nm for AgNPs (curve 1) and 540 nm for AuNPs (curve 5). The appearance of absorption spectra having single surface plasmon band is indicative of the possible formation of Au-Ag nanoparticles rather than the reaction mixture containing the monometallic nanoparticles of Au and Ag or reaction mixture containing more number of Au (core)-Ag (shell) nanoparticles.

Figure 1: UV-Vis Absorbance Spectra of the 5 Samples Ag, Ag:Au (3:1), Ag:Au (1:1), Ag:Au (1:3) and Au



3.2 FESEM and TEM Studies

The micrographs obtained for sample Ag:Au (1:1) using FESEM and TEM are shown in figure 2a and figure 2b & 2c respectively. No much information can be obtained from the FESEM images. From the TEM images, the formation of Au (core)-Ag (shell) nanoparticles as well as Ag-Au alloy nanoparticles can be seen. There is a clear contrast between the Au and Ag with the darker regions corresponding to Au and less darker regions corresponding to Ag. Similar results were reported in the literature [16]. The presence of both Au and Ag component is visible from EDX spectrum of Ag:Au (1:1) sample as seen in figure 3.

Figure 2: (a) FESEM Micrograph of Sample Ag:Au(1:1) (b) and (c) TEM Micrographs of Sample Ag:Au(1:1)

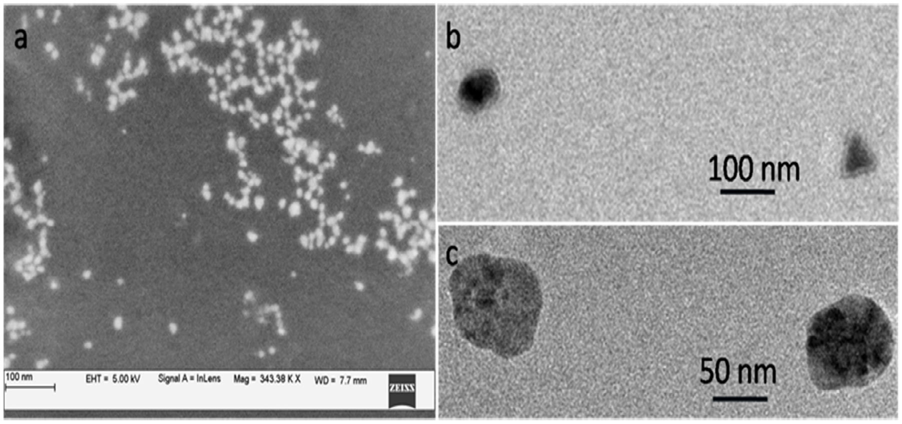
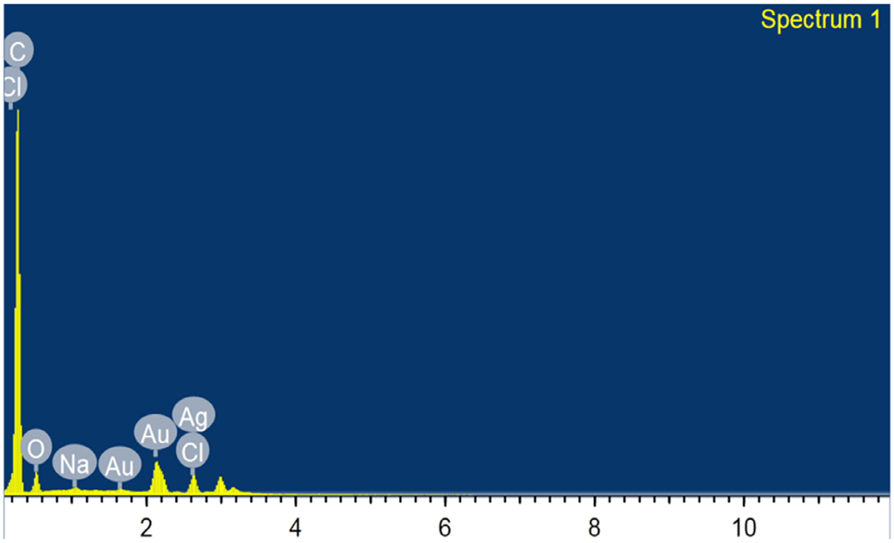


Figure 3: EDX Spectrum of Ag:Au(1:1) Sample



4. Conclusion

Synthesis of Au-Ag nanoparticles using *Melastoma malabathricum* flower extract was investigated. During the formation of AuNPs alone, quick reduction of Au^{3+} was observed at room temperature where as the formation of AgNPs under the similar experimental conditions was found be very slow thereby implying the slower reduction of Ag^{+} ions. Owing to these observations, expected the formation of Au (core)-Ag (shell) nanoparticle rather than the Au-Ag alloy nanoparticles. But the presence of single SPR peak in UV-Vis absorbance spectra was indicative of the formation of Au-Ag alloy nanoparticles and not the Au(core)- Ag (shell) nanoparticles. TEM micrographs also revealed the formation of Au-Ag alloy nanoparticles in addition to few Au (core)- Ag (shell) nanoparticles. The synthesized nanoparticles can be utilized for various applications such as catalysis, SERS studies, nonlinear optics etc.

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