



Green synthesis of mixed metallic nanoparticles using room temperature self-assembly

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ABSTRACT

Bimetallic nanoparticles of silver (Ag) and gold (Au) were synthesized at room temperature using Curcumin. Reduction process of silver and gold ions with different molar ratios leads to production of different nanostructures including alloys and core-shells. Produced nanoparticles were characterized simultaneously with FTIR, UV/vis. spectroscopy, transmission electron microscopy (TEM), and Energy-dispersive X-ray (EDAX). UV/vis. optical absorption spectra of as synthesized nanoparticles reveals presence of surface plasmon resonance (SPR) of both silver at (425 nm) and gold at (540 nm) with small shift and broadness of gold band after mixing with resucing and capping agent in natural extract which suggest presence of bimetallic nano structure (Au/Ag). FTIR and EDAX data approve the presence of bimetallic nano structure combined with curcumin extract. TEM micrographs shows that silver and gold can be synthesized separately in the form of nano particles using curcumin extract. Synthesis of gold nano particles in presence of silver effectively enhance and control formation of bi-metallic structure.

Keywords

Silver nanoparticles; gold nanoparticles; Bimetallic nanoparticles; X-ray diffraction; transmission electron microscopy; Bimetallic nanoparticles; Ag/Au; TEM; XRD; EDAX

1- INTRODUCTION

During last decade green synthesis of metallic nanoparticles are of increasing interest while preparation of bimetallic or multi-metallic nanoparticles NPs usually involves formation of core/shell and/or alloy type structures that possess an improved physicochemical character compared with their monometallic counterparts [1, 2].

Bimetallic and tri-metallic NPs have industrial and scientific importance result from novel properties including optical, magnetic and electronic properties suitable for practical applications [3]. Bimetallic NPs usually synthesized by chemical reduction, templet synthesis, laser ablation and seed-mediated growth that characterized by a well dispersed pattern in presence of stabilizers and/or surfactant. Bimetallic nanoparticles known to exhibit higher potential than mono-metallic counterparts and evidenced to be an effective catalysts for selective oxidation of glucose to gluconates compared to enzymatic catalysis in addition to operation in a wide range of pHs [4-6].

A growing concerns devoted to green synthesis necessitate the enhancement of new and eco-friendly regimes. Recently, many distinct approaches have been reported for production of different size and shape NPs. [7]. Because of the inherent advantages such as eco-friendly and nontoxic, low cost and process simplicity biogenic approaches using phytochemicals using various plant bio-sources attract researcher's attention especially for Au containing Ag and Au NPs. [8].

Distribution modes of the two elements comprising the bimetallic nanoparticle (BNPs) define their structure since it can be oriented in random alloy, core-shell, cluster-in cluster or alloy with intermetallic compound. Many factors controlling size and shape of prepared nanoparticles in the form of mono or bimetallic NPs including preparation techniques and conditions of preparation (pH, temperature, pressure or surround). Monometallic nanoparticles (MNPs) can be shaped in different forms depending on application needed or method and condition of preparation. These shapes includes mainly spheres, cubes and rods in addition to tetrahedrons, octahedron, truncated octahedrons, and even stars while combination of two or more metals in the nano form may results in much more opportunities in shape and structure due to mixed distribution of each metal and their various organization [9].

Medecinal plants are known to serve as a basic source of a variety of bioactive phytochemicals. These phytochemicals serve as reducing, capping and even stabilizing agent in bioreduction and stabilization of phytochemical nanoparticles with immense therapeutic properties. Among these plant, Curcumin a as a household remedy to many ailments and considered as a highly bioactive, nontoxic and potent agent found in turmeric [10,11].

Present work aims to introduce a new and simple route for preparation of mono and bimetallic nanoparticles using eco friendly method i.e. green synthesis with available plant extract of curcumin and extended for characterization of these NPs for possible use in various medical application and devoted mainly for breast cancer treatment.

2. MATERIALS AND EXPERIMENTAL WORK

2.1. Materials

The Curcuma longa was purchased from a local market in (Riydh, KSA). HAuCl₄ was purchased from Sigma-Aldrich (Poole, UK). Tetrachloroauric (III) acid trihydrate (HAuCl₄·3H₂O, 99.5% GR of analysis) was obtained from Merk, Germany. The Silver nitrate (AgNO₃) was obtained from Sigma-Aldrich chemicals. All solutions were freshly prepared using distilled water and kept in the dark to avoid any photochemical reactions.

2.2. Green synthesis of AuNPs and AgNPs

0.5 g of Curcuma longa was added to 100 mL deionized water. The mixture was kept at room temperature (25°C) for about 4 hours. The solution was filtered and centrifuged to obtain clear solution. Filtrate was used as a green reducing and stabilizing agent. 50ml of the extract was mixed with 100 ml of the aqueous solution of (1mM) HAuCl₄ under constant and vigorous stirrer for 24 hours. The change in color was observed from colorless to light purple which indicating the reduction of gold and formation of gold nanoparticles. Same proceddure was employed for synthesis of both silver nanoparticle and bimetallic nanoparticles of silver (Ag) and Gold (Au). Figure 1 introduce a simple and short schematic presentation for the preparation process.



Figure 1 Schematic presentation of preparation process.

2.3. Characterization Techniques

X-ray diffraction (XRD) patterns were recorded via PANalytical X'Pert PRO using Cu K α radiation and operating potential of 30 kV within Bragg's angle (2θ) ranging 4-80°. Nicolet iS10 single beam spectrometer was used for recording Fourier transforms infrared spectra in the spectral range (4000-400) cm^{-1} . UV/Vis. were measured in the wavelength range 190-900 nm using JASCO double beam spectrophotometer V-570 UV/VIS/NIR to manifest particle size and distribution and to retrace changes in their optical properties. Particle size distribution and the shape was also investigated using JEOL JEM 2100 Japan (TEM) "Transmission Electron Microscope" worked at accelerated voltage of 160 kV. The surface charge of the gold nanoparticles in various solutions was measured by using a zeta potential analyzer by used Zetasizer APS Essentials manual UV Instruments Ltd. Enigma Business Park, Grovewood Road, MAN0426-1.0/ MAN0429-1.0 United Kingdom. Silver and gold concentrations measurements were studied via atomic absorption, where silver and gold concentrations were found to be 380 and 460 ppm respectively.

3. RESULTS AND DISCUSSIONS

3.1. UV-Vis. Optical Studies for (Ag NPs/Au NPs) and Mixed Nanoparticles

Figure 2 depicts UV/Vis. optical absorption spectra in the range of 200-1100 nm for as prepared Ag, Au and mixed nanoparticles. Obtained spectra shows the characteristic band represent the surface plasmon resonance (SPR) characterized both AgNPs and AuNPs in their position 425, 540 nm respectively as indicated by several authors [12-14]. An addition strong UV absorption bands were observed at about 220-250 nm that may be attributed to residual of plant extract used in the process of synthesis or trace iron impurities even that appears even in ppm level [15] without any evidence for any visible band till the end of measurements.

Preparation of bimetallic nanoparticles of Au/Ag usually involve shift and/or overlap of SPR absorption bands combined with a decreases in intensity of the broad band indicating formation of spherical homogeneous distribution of Gold and silver nanoparticles [16]. The small position shift, weakend and broadening in SPR band of bi-metallic nanoparticle spectra attributed to the increase of gold mole fraction and indicates formation of bi-metallic dispersed nano-structure.

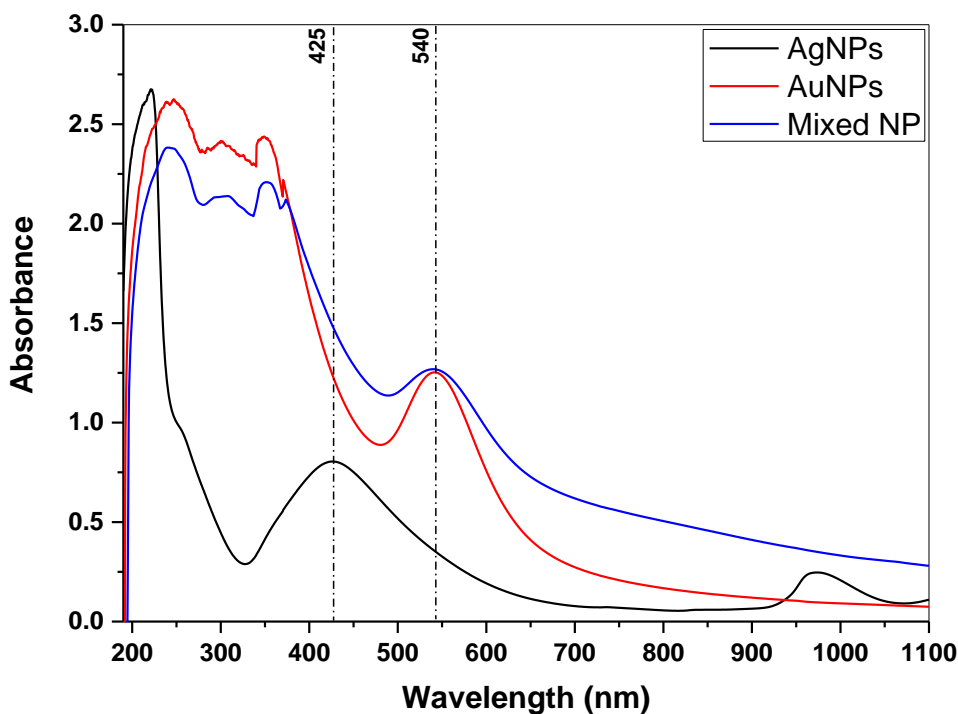
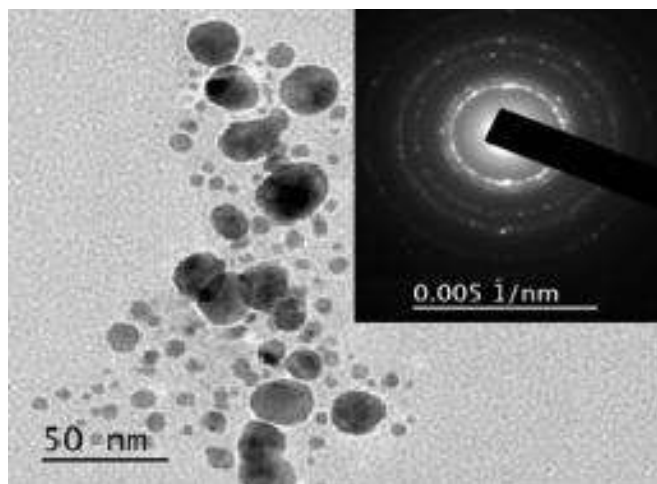


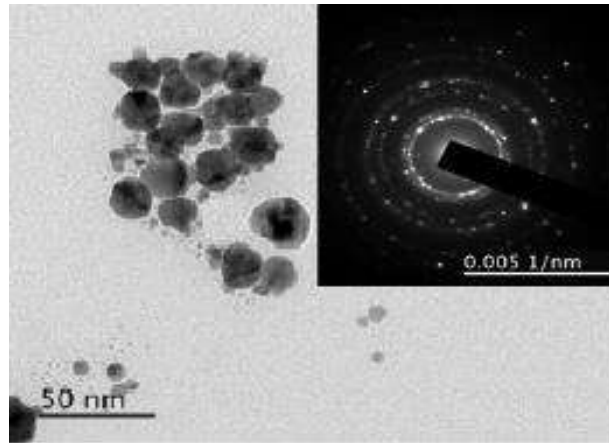
Fig. 2. UV/Vis. spectra for Ag, Au and mixed synthesized nanoparticles

3.2. Transmission Electron Microscopy and Zeta potential studies

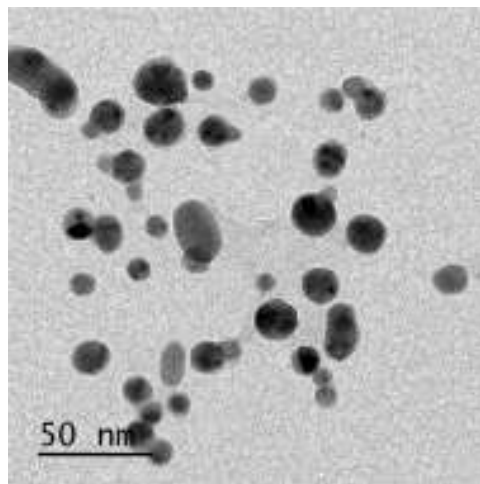
Figure 3 reveals transmission electron microscopy (TEM) images of as synthesized silver, gold and their bi-metallic nanoparticles respectively. It was clear that particle are uniformly distributed and well dispersed. The size of prepared silver nanoparticles was found to be ranged 15-25 nm (Figure a) while that of gold swing from 10-30 nm (Figure b). It was found that addition of silver to gold effectively control the size and shape of produced bi-metallic nano-structure and it was in agreement with the data obtained from the UV/vis. Optical absorption spectra. The obtained bi-metallic nanoparticle was found to be in the range 8-15 nm with variable geometry.



(a)



(b)



(c)

Figure 3 TEM images of as synthesized (a) silver, (b) gold and (c) their bi-metallic nanoparticles

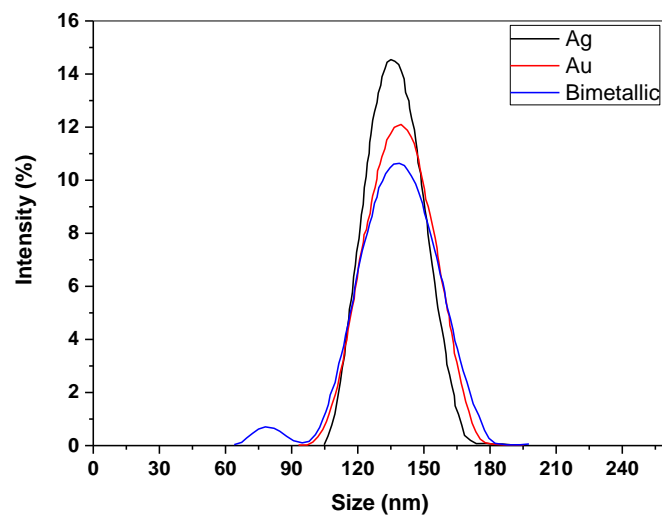


Figure 4 Zetasizer for the silver, gold and their bi-metallic nanoparticles

Figure 4 show Zetasizer for the silver, gold and their bi-metallic nanoparticles respectively which indicates the non monodispersed state due to the negatively charged layer. This non monodispersity accounts for the probe preparation



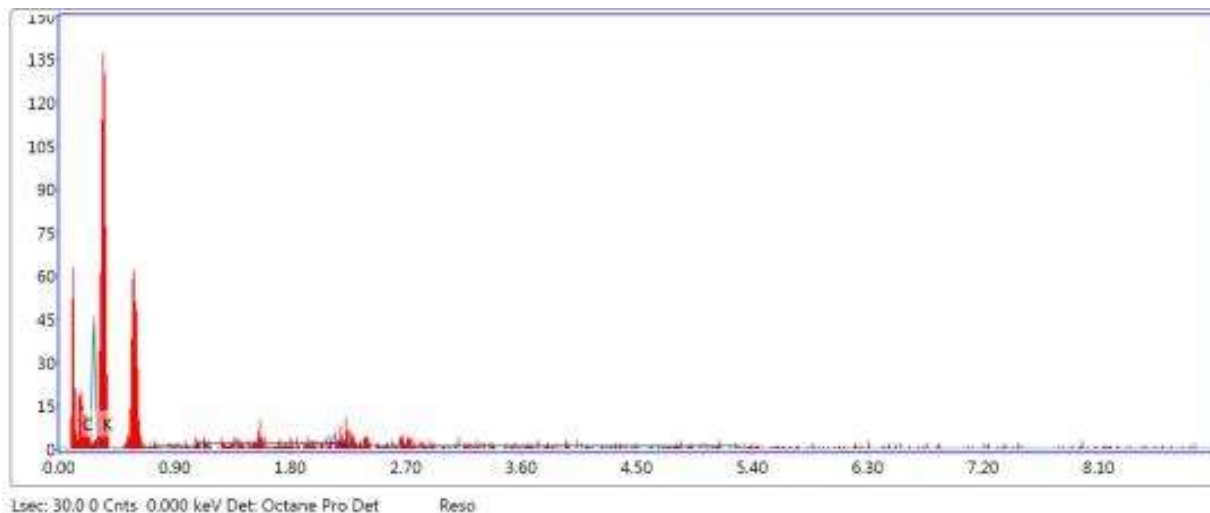
and generation of color signal in chromatographic strip assay. Surface potential of synthesized nanoparticles were performed to measure electrophoretic mobility based on dynamic light scattering (DLS) of both bare and antibody conjugated Ag and Au nanoparticles. Obtained negative value of Zeta potential for all samples indicate presence of stable nano-sized particles [17].

3.3. EDX analysis

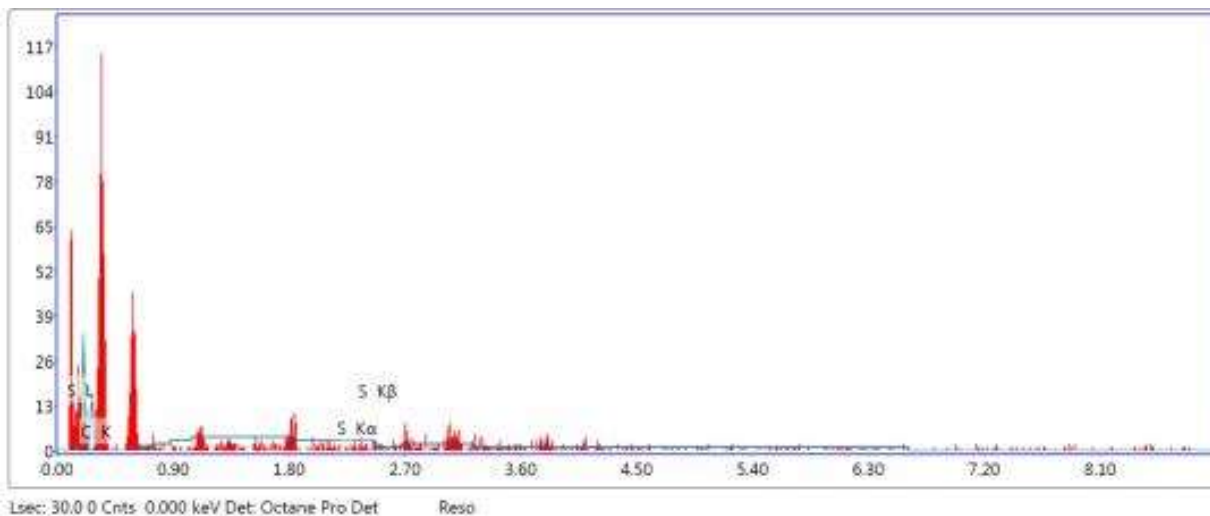
Energy dispersive X-ray was used to identify basic component of synthesized sample and their relative weights. It was found that carbon from used plant extract is the basic component that represent major fraction of samples and the remind assigned to silver, gold and bimetallic nanoparticles as indicated in table (1). In addition the prence of certain maxima at specified energies shown in Figure 5 point to the presence of synthesized particles in the nano-scale.

Table (1) weight percent of basic constituents of synthesized nanoparticle using Curcamine extract

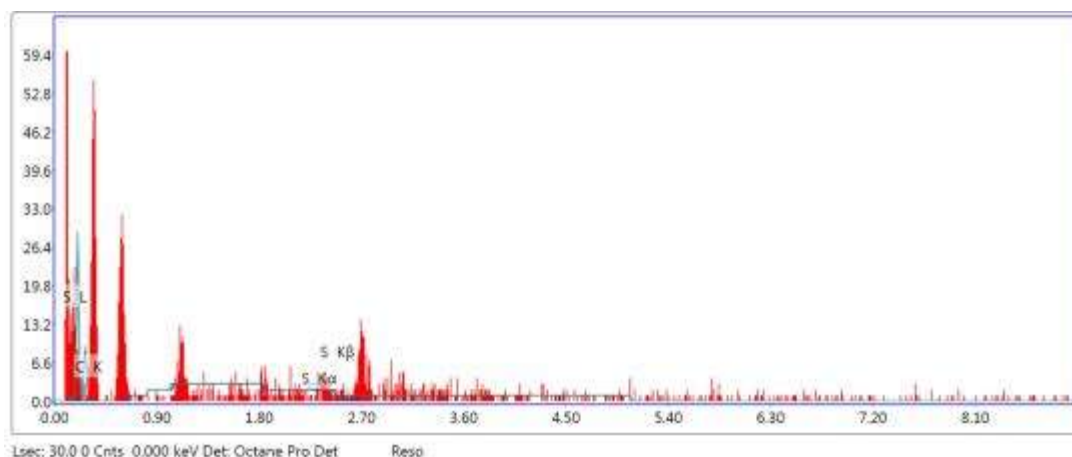
Sample	C	Au	Ag
	Wt %		
AgNPS	92.75	00.00	7.25
AuNPs	61.94	38.06	0.00
Bi-metallic	85.25	11.73	3.02



(a)



(b)



(c)

Figure (5) EDX analysis of Gold (a), Silver (b) and Bimetallic nanoparticles (c).

4. CONCLUSIONS

An effective green synthesis, eco-friendly regime for silver, gold or bimetallic nanoparticles synthesis based on Curcamine plant extract were developed indicated through SPR appers at 425nm for AgNPs and at 540 nm for AuNPs. During synthesis of bi-metallic nanoparticled AgNPs considered to act as a seed-growth for AuNPs. These previous results supported by TEM image and Zeta potential measurements. It was found that size and distribution of gold through bimetallic one can be controlled via AgNPs.

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