

Green Synthesis of Ag, Au, and Au-Ag Bimetallic nanoparticles using *Chrysophyllum albidum* Aqueous Extract for Catalytic Application of Electro-Oxidation of Methanol.

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ABSTRACT

Green synthesis of Au, Ag, and Au-Ag bimetallic nanoparticles was achieved by the reduction of gold and silver metal salts using an aqueous extract of *Chrysophyllum albidum*, by a microwave technique. The optical properties of the metal and bimetallic heterostructures are reported. The morphology of the particles was regular with a dominant quasi spherical morphology. Catalytic properties of the nanoparticles were investigated in the direct methanol fuel cell electro-oxidation under acidic conditions by cyclic voltammetry measurements at room temperature. The Au-Ag nanoalloy showed improved catalytic activity and stability at low electrode potential towards methanol oxidation.

(Keywords: *Chrysophyllum albidum*, green nanoelectrocatalyst, nanostructures, catalytic properties, X-ray diffraction, transmission electron microscopy. TEM)

INTRODUCTION

There has been a rise in global energy demands in the last five decades as a result of exponential increase in industrialization. There has been less dependence on fossil fuel technology as a reliable energy source due to huge operational cost and harm to the environment (Zhong *et al.*, 2010).

As an energy conversion system, the direct methanol fuel cell (DMFC) technology offers numerous advantages such as high energy density, light weight, compact foot print, low

pollution, simplicity as well as easy and fast recharging capabilities, especially for portable devices (Gan *et al.*, 2013; Hockadey *et al.*, 2000; Khantimerov *et al.*, 2013).

One of the most important challenges for fuel cell commercialization is the preparation of active, robust and low-cost electrocatalysts. Poor activity of the catalysts at the anode of a DMFC often leads to a loss of about one-third of the available energy (Mehta and Cooper, 2003). The relatively high cost and propensity towards poisoning of platinum by the CO species are also drawbacks of the well-studied platinum catalysts (Hua *et al.*, 2013; Huang *et al.*, 2013; Rudi *et al.*, 2014).

Consequently, there has been an interest in the synthesis and electrocatalytic alcohol oxidation action of other mono-, bi- and trimetallic nanoalloys or core shell nanoparticles which function as catalysts with enhanced selectivity, activity and stability (Cui *et al.*, 2013; An *et al.*, 2013; Wang *et al.*, 2014) Pt/Ru colloid catalysts of different compositions was demonstrated by Dubau *et al.* (2003) via co-reduction/direct mixing of platinum and ruthenium salts in the presence of tetraoctylammonium triethylhydroborate as the reducing agent.

Ruthenium rich catalysts (50:50 composition) gave the best results at high temperature for the electrooxidation of methanol under acidic conditions. Tan and co-workers (2012) synthesized Au-Pt bimetallic core-shell nanoparticles by the ascorbic acid reduction of

the metal salts in organic solvents. The improvement in catalytic properties was attributed to variation in metallic alloy composition, particle size and electronic effect.

Although there has been an increase in the number of publications involving the synthesis and applications of metallic and bimetallic nanoparticles using plant materials, little emphasis has been placed on their usage as green nano-electrocatalysts in alcohol fuel cell oxidation (Mittal *et al.*, 2013; Dare *et al.*, 2015; Song *et al.*, 2010). Green nano-electrocatalysts are relatively cheap, with simple synthetic routes that eliminates the use of toxic solvents/reagents. In this paper, we present for the first time, a rapid green synthesis of Au, Ag, and Au-Ag bimetallic nanoparticles (or nanoalloys) using *C. albidum* aqueous extract, and their application as cheap and effective “green nano-electrocatalysts” towards the electrooxidation of methanol

EXPERIMENTAL

Chemicals and Plant Material

Fresh leaves of *Chrysophyllum albidum* were collected from a local residence in Ibadan, Nigeria in 2009. Gold (III) Chloride trihydrate (99.9%), silver nitrate (99.2%) was procured and used as received from Sigma Aldrich.

Preparation of Leaf Extract

Chrysophyllum albidum leaves was washed with deionised water and air-dried in a fume hood for two weeks. Finely cut leaves were boiled in deionised water (1:10 w/v) for 20 min and extract filtered by a Whatmann filter paper. The filtrate was cooled to room temperature and refrigerated at 4 °C.

Microwave Assisted Biosynthesis of Au and Ag Nanoparticles

4 mL of 0.1 g/mL aqueous filtrate of the extract was reacted with 8 mL of 1 mM silver nitrate and gold (III) chloride trihydrate solutions in two centrifuge tubes respectively, exposed to microwave irradiation using a DEFY model DMO 35338I microwave at low operating power level 1 for 90 s. The resulting Ag and Au metal nanoparticles were obtained by centrifugation at

4000 rpm for 5 mins and purified by re-suspending in methanol and finally centrifuged at 4000 rpm for 2 min.

Microwave Assisted Biosynthesis of Au-Ag Bimetallic Nanoparticles

0.5 mL of 0.1 g/mL aqueous filtrate of the plant extract was mixed with 10 mL, of 1 mM mixture of AgNO₃ and HAuCl₄·3H₂O solutions in a centrifuge tube was exposed to microwave irradiation, using a DEFY model DMO 35338I microwave at low operating power level 1 for 90 s. The final volume ratio of extract and metal salts was 1:10:10. The Au/Ag bimetallic nanoparticles were collected by centrifugation at 4000 rpm for 5 min and purified by re-suspending in methanol and finally centrifuged at 4000 rpm for 2 min.

Optical Characterization

A Perkin-Elmer Lambda 20 UV-vis spectrophotometer was used to carry out absorption measurements in the 200–800 nm wavelength range. Aliquots of biosynthesized nanoparticles were placed in quartz cuvettes (1 cm path length) and the absorbance recorded between 10-60 min to monitor the bio-reduction process.

Characterization of the metal nanoparticles

Samples for transmission electron microscopy (TEM) analysis were prepared by placing an aliquot of the nanoparticles onto an amorphous carbon substrate supported by a copper grid and then allowing the solvent to evaporate at room temperature. The morphology and particle sizes of the samples were characterized using a JEOL 1010 TEM at an accelerating voltage of 100 kV. Pictures were captured using a Megaview III camera and imaged using Soft Imaging Systems iTEM software.

Detailed morphological and structural features were investigated using high-resolution transmission electron microscopy (HRTEM) on a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV. X-ray diffraction patterns of the nanoparticles were obtained using Bruker

D8 Advance X-ray powder diffractometer with Cu K α (1.5418 Å) radiation at 40kV and 30mA.

Electrochemical Measurements

Electrochemical experiments were conducted in a conventional three electrode cell using BASi EC Epsilon workstation (BASi Analytical Instruments) at room temperature following the method of Tan *et al.* (2012) with little modifications. Platinum foil and a Ag/AgCl electrode were used as the counter and reference electrodes respectively. A glassy carbon (GC) disk coated with Au-Ag nanoparticle catalyst was employed as the working electrode. The glassy carbon (GC) electrode was polished with 0.3 μ m Al₂O₃ slurry and washed ultrasonically with deionised water before use.

The electrode reaction was conducted in a N₂-saturated 0.5 M H₂SO₄ solution containing 0.5 M CH₃OH. The working electrode was prepared by treating 0.1014 mg Au metal and Au-Ag bimetallic nanoparticles separately, suspended in a 1 mL mixture of isopropyl alcohol and millipore water (1:1 v/v) and then ultrasonically blended for 30 min to form a homogenous catalyst ink. A sample of 20 μ L of the ink was pipetted onto the GC surface. The working electrode surface was covered with 10 μ l Nafion solution (5%) as a binding material and left to dry under atmospheric pressure for 30 min.

The catalyst loadings for each of Au metal nanoparticles and Au-Ag nanoalloy was 28.56 μ g/cm². The activity and stability of the nanoparticles catalysts towards electro-oxidation of methanol in an acidic medium were determined by cyclic voltammetry (CV) measurement at scan rates of 50 mV/s, 100 mV/s and 200 mV/s and an applied voltage range of -0.6V to 0.6V.

RESULTS AND DISCUSSION

Optical Properties of the Au, Ag and Au-Ag Bimetallic Nanoparticles

The optical properties of the biosynthesized nanoparticles are shown in Figure 1. The metal nanoparticles exhibited distinct surface plasmon resonance (SPR) effect which is due to the collective oscillation of free conduction electrons induced by an interacting electromagnetic field (Mulvaney, 1996). Rapid formation of nanocolloids

was achieved upon exposure of reaction media to microwave irradiation. This might be due to increased homogenous thermal agitation and nucleation growth of nanoparticles (Creighton *et al.*, 1979).

From Figure 1a, fine, narrow absorption peaks occurred at 530–560 nm corresponding to the SPR band of gold nanoparticles. This was confirmed by the appearance of a purple colour in the reaction medium (Figure 1b). The peak intensity increased gradually as a function of reaction time from 10 - 60 minutes. In the case of silver nanoparticles, absorption peaks were observed between 430-450 nm (Figure 1c). The presence of a SPR band at this wavelength range indicated the formation of Ag nanoparticles (Daisy, 2009). Absorbance intensity increased steadily from 15 min and was highest after 60 min (Figure 1c). A gradual colour change from a colourless Ag⁺ solution to a brown colour signalled the formation of silver nanoparticles (Figure 1d).

For the Au-Ag bimetallic nanoparticles, absorption peak between 520–560 nm were observed (Figure 2a), corresponding to the SPR band of Au-Ag. This was confirmed by the appearance of a dark purple colour in the reaction medium (Figure 2b). The peak intensity increased gradually as a function of reaction time from 10 - 45 minutes indicating an increase in the nanoparticles concentration.

Characterization of Metal Nanoparticles

From the X-ray diffraction studies, the nanoparticles exhibited the face centred cubic (fcc) crystal phase. The diffraction peaks for the gold nanoparticles (Figure 3a) were observed at $2\theta = 38.48^\circ, 44.63^\circ, 64.98^\circ, 77.86^\circ, 82.16^\circ$ corresponding to the (111), (200), (220), (311) and (222) facets of cubic gold respectively. For the silver nanoparticles (Figure 3b), peaks appeared at 2θ values of 38.01° (111), 44.29° (200), 64.04° (220), 77.85° (311) which is characteristic of the face centred cubic crystal phase. The Au-Ag bimetallic diffraction pattern (Figure 3c), displayed peaks at $2\theta = 38.40^\circ, 44.25^\circ, 64.72^\circ, 75.89^\circ, 81.23^\circ$ corresponding to the (111), (200), (220), (311) and (222) facets of fcc crystalline phases.

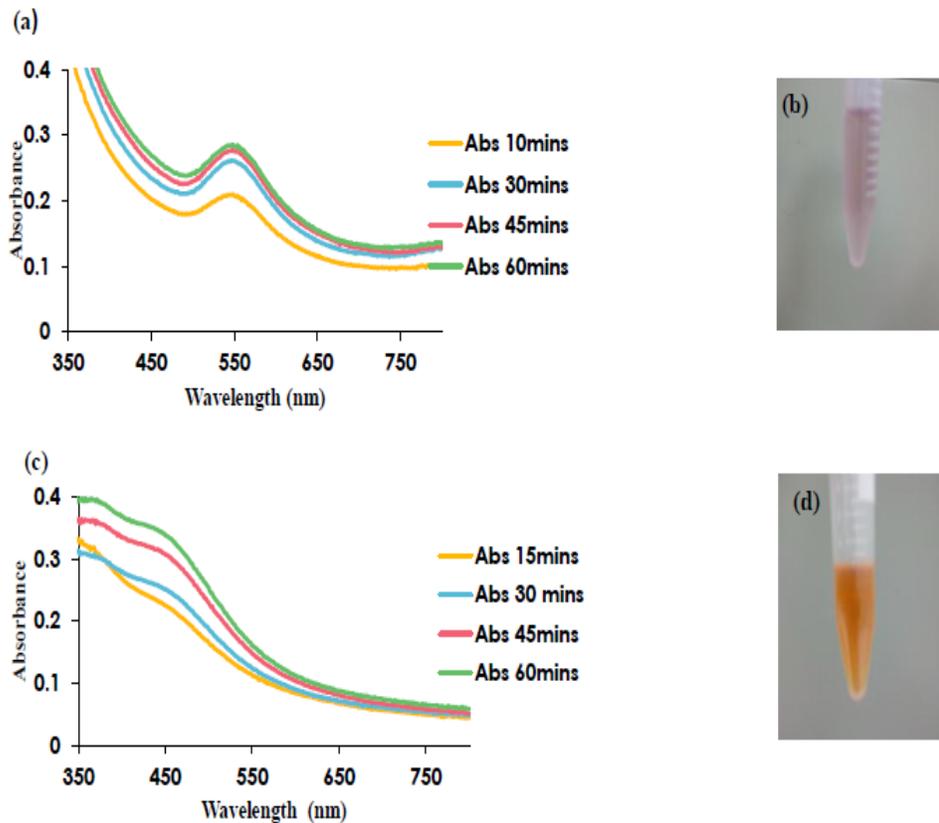


Figure 1. UV/Vis Spectra of Microwave Assisted Biosynthesized Nanoparticles using 1mM Metal Salt Concentration and Irradiation time of 90 seconds: (a) Au nanoparticles, (b) purple colour of Au nanoparticles, (c) Ag nanoparticles and (d) deep brown colour of Ag nanoparticles

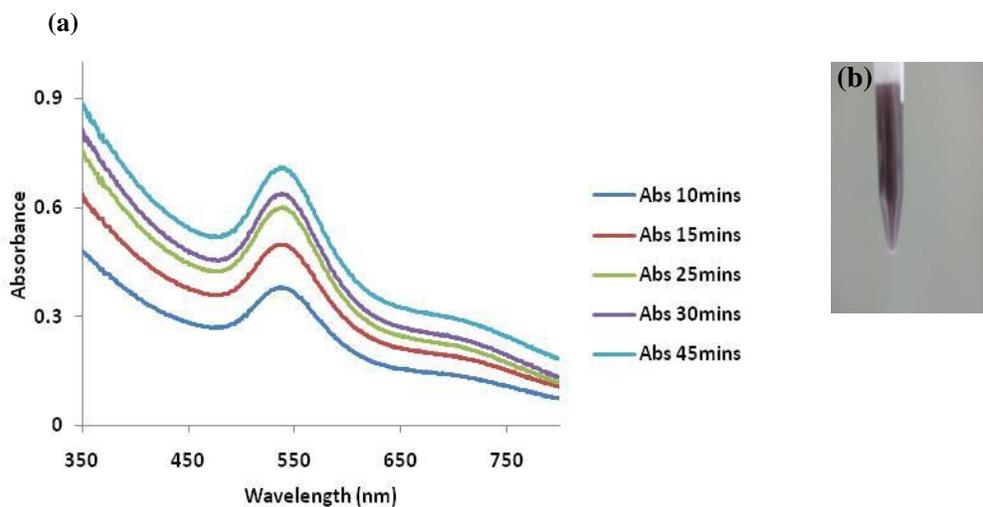


Figure 2: UV/Vis Spectra of Microwave Assisted Biosynthesized using 1mM Metal Salts Concentration (1:1 v/v ratio) and Irradiation time of 90 seconds: (a) Au -Ag bimetallic nanoparticles and (b) deep purple colour of Au -Ag bimetallic nanoparticles

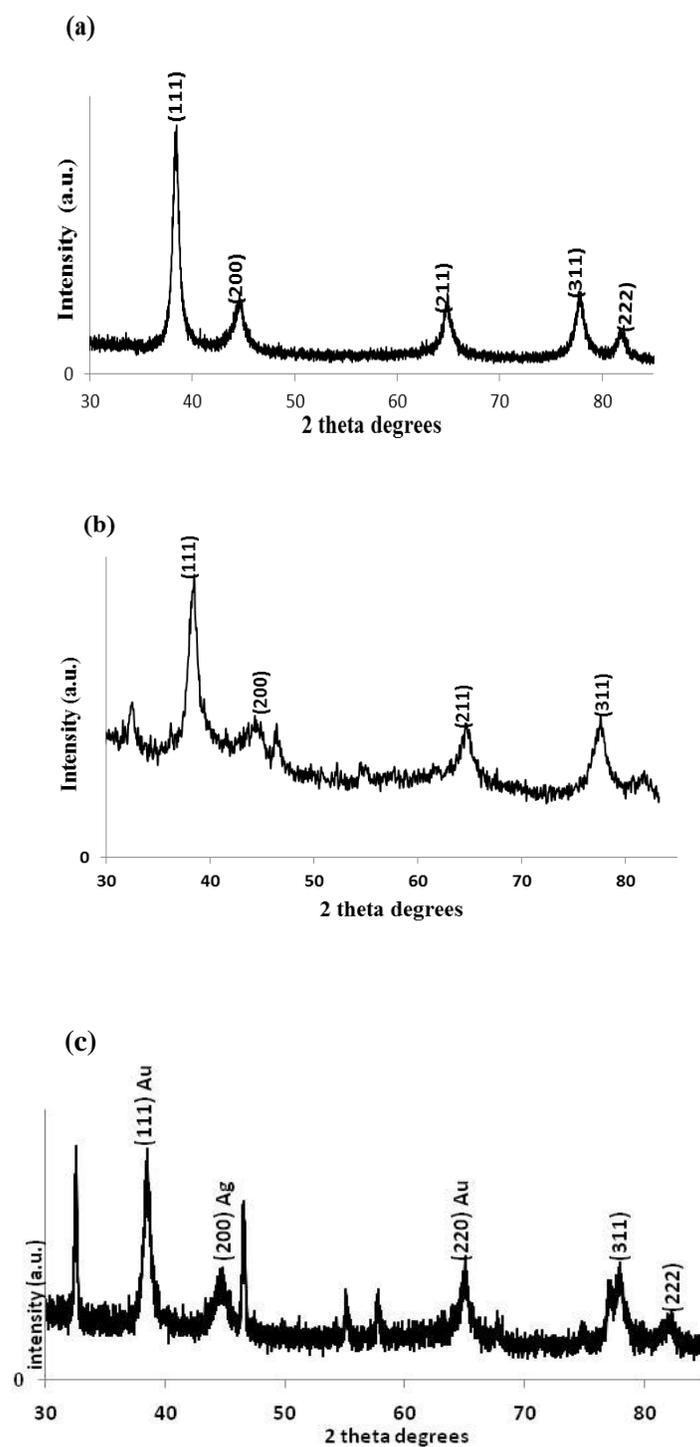


Figure 3: XRD Patterns of Microwave Assisted Biosynthesized: (a) Au nanoparticles (b) Ag nanoparticles (c) Au-Ag bimetallic nanoparticles.

The diffraction peak at 44.25° was due to Ag metal while the peaks at 38.40° (111) and 64.72° (220) were attributed to the Au metal in the nanoalloy (Figure 3c).

The TEM and HRTEM images of the nanoparticles revealed particles with uniform quasi-spherical morphology. The particle size ranges were 14-17 nm, 31-45 nm and 25-35 nm for Au and Ag (Figure 4) and Au-Ag bimetallic nanoparticles (Figure 5a), respectively.

Ali *et al.* (2011) obtained similar morphology and size range for gold nanoparticles. Lattice fringes were not clearly visible in the HRTEM images of gold nanoparticles (Figure 4b) while for silver nanoparticles, the HRTEM image showed a single particle with lattice fringes and d-spacing of 0.29 nm (Figure 4d).

HRTEM images of the Au-Ag nanoalloy (Figure 5b) showed clear lattice fringes with a d-spacing of 0.36 nm.

A detailed phytochemical screening of the aqueous *C. albidum* extract confirmed the presence of tannin, saponin, alkaloids, terpenoids, carbohydrate, polyphenol, etc (Table1).

CYCLIC VOLTAMMETRY STUDIES

Electrocatalytic Activity of Au and Au-Ag Nanoalloy Catalysts for Methanol Oxidation

The cyclic voltammogram (CV) of electrooxidation of methanol by Au metal nanoparticles and Au-Ag

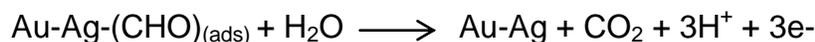
nanoalloy catalysts in 0.5M H₂SO₄ at room temperature was obtained at a scan rate of 100mV/s between -0.6V to +0.6V vs Ag/AgCl electrode as shown in Figure 6.

Methanol oxidation did not take place in the presence of Au nanocatalyst. However, in the case of the Au-Ag nanoalloy catalyst, two peaks corresponding to the adsorption/desorption of hydrogen and oxidation/reduction were observed in the forward and backward sweeps which is characteristic of CV curves for methanol oxidation (Anindita *et al.*, 2011).

The oxidation peak current density ($I_{p,i}$) value of 38.24 μ A/cm² was obtained at 0.325V in the forward sweep while a less prominent peak current density value ($I_{p,b}$) of -11.65 μ A/cm² was recorded at -0.002V in the backward sweep. Usually, the onset of potential and current density are the two important parameters to compare the activities of electrocatalysts for the electro-oxidation of methanol or formic acid (Chen *et al.*, 2006).

The higher current density on Au-Ag nanoalloy at lower potentials indicated enhanced methanol oxidation catalytic activity. This result of this study is comparable with those reported on Pt/Ru and AuPtPd alloy nanoparticles catalysts (Sebastiana *et al.*, 2013; Moreira *et al.*, 2012; Zhu *et al.*, 2012).

A proposed scheme of the overall reaction processes occurring in the electrode cell is:



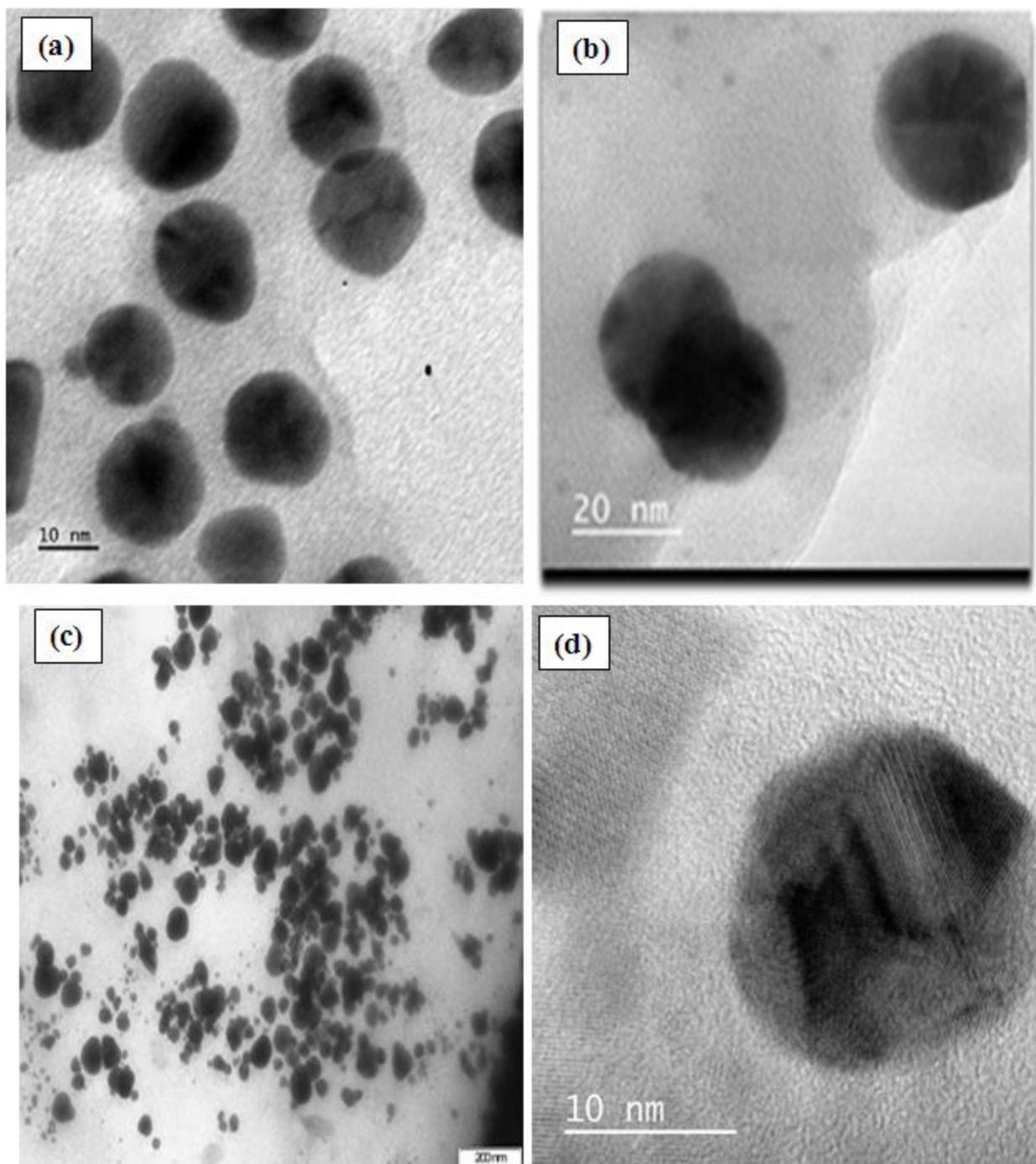


Figure 4: (a) TEM images of microwave assisted biosynthesized Au nanoparticles using 1mM metal salt concentration and irradiation time of 90 seconds, (b) corresponding HRTEM image of Au nanoparticles (c) TEM images of microwave assisted biosynthesized Ag nanoparticles using 1mM metal salt concentration and irradiation time of 90 seconds and (d) corresponding HRTEM image.

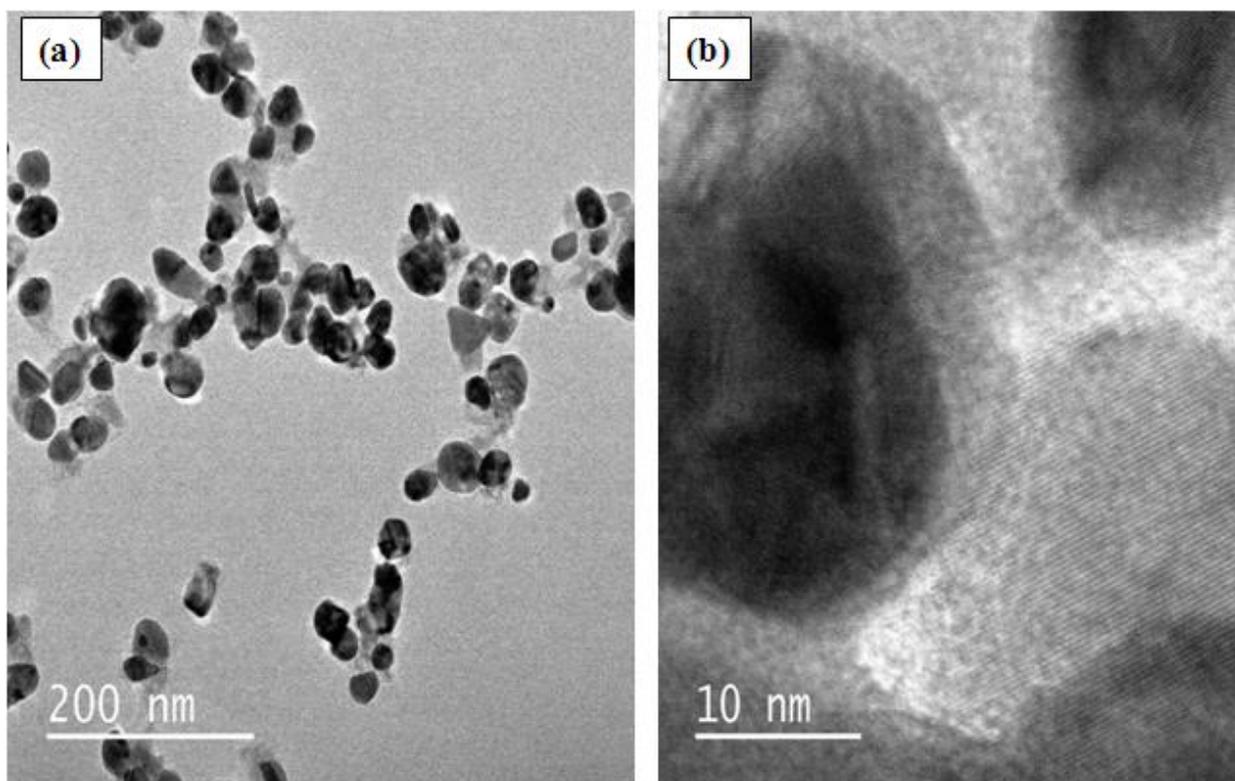


Figure 5: (a) TEM image of microwave assisted biosynthesized Au-Ag bimetallic nanoparticles using 1mM metal salts concentration and irradiation time of 90 seconds and (b) corresponding HRTEM image of Au-Ag bimetallic nanoparticles.

Table 1: Phytochemical Screening of *C. albidum* Aqueous Extract.

s/no	Phytochemicals	Present (+)/Absent (-)
1	Alkaloids	+
2	Terpenoids	+
3	Flavonoids	+
4	Saponin	+
5	Cardiac glycosides	+
6	Total polyphenol	+
7	Carbohydrate	+
8	Protein	+
9	Tannin	+

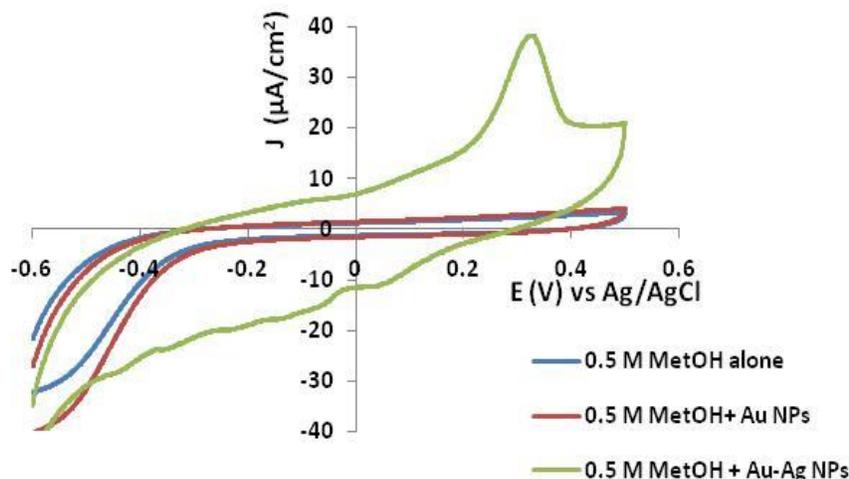


Figure 6: Cyclic Voltammogram of 0.5 M Methanol: alone, in the Presence of Au Nanoparticles.

The enhancement in catalytic activity is due to the electronic and chemical properties of the additional Ag atoms in the alloy. The presence of silver atoms facilitated the adsorption of methanol molecules by Au atoms in the alloy and the adsorption of oxygen containing species such as

water molecules. The Ag atoms influenced adsorption of water molecule at a low potential and contributed towards the oxidation of the poisoning CO intermediate based on the reaction:



A high ratio of $I_{p,f} : I_{p,b}$ (3.28) observed for the Au/Ag alloy catalyst further indicated a better poisoning tolerance towards methanol oxidation.

A plot of the peak current density (J_p) values against square root of scan rates (50mV/s, 100mV/s and 200mV/s) revealed a near linear curve (Figure 7a) showing that the process of electro-oxidation of methanol is diffusion-controlled (Nicholson and Shain, 1964). For a reversible reaction at 25 °C the peak current, I_p , can be computed referring to the Randles–Sevcik equation (Bard and Faulkner, 2001).

$$I_p = 2.69 \times 10^2 AD^{1/2} n^{3/2} \nu^{1/2}$$

where I_p is the peak current, A is the electroactive area, D is the diffusion coefficient of the analyte, n is the number of electrons involved in the redox reaction, ν is the scan rate, and C is the concentration of the redox (methanol) molecules in solution (0.5 M). The electroactive area (A) was obtained from the slope of the peak cathodic current (I_{pc}) versus the square root of the scan rates at 0.5 M methanol concentration (Bard and Faulkner, 2001) (Figure 7b).

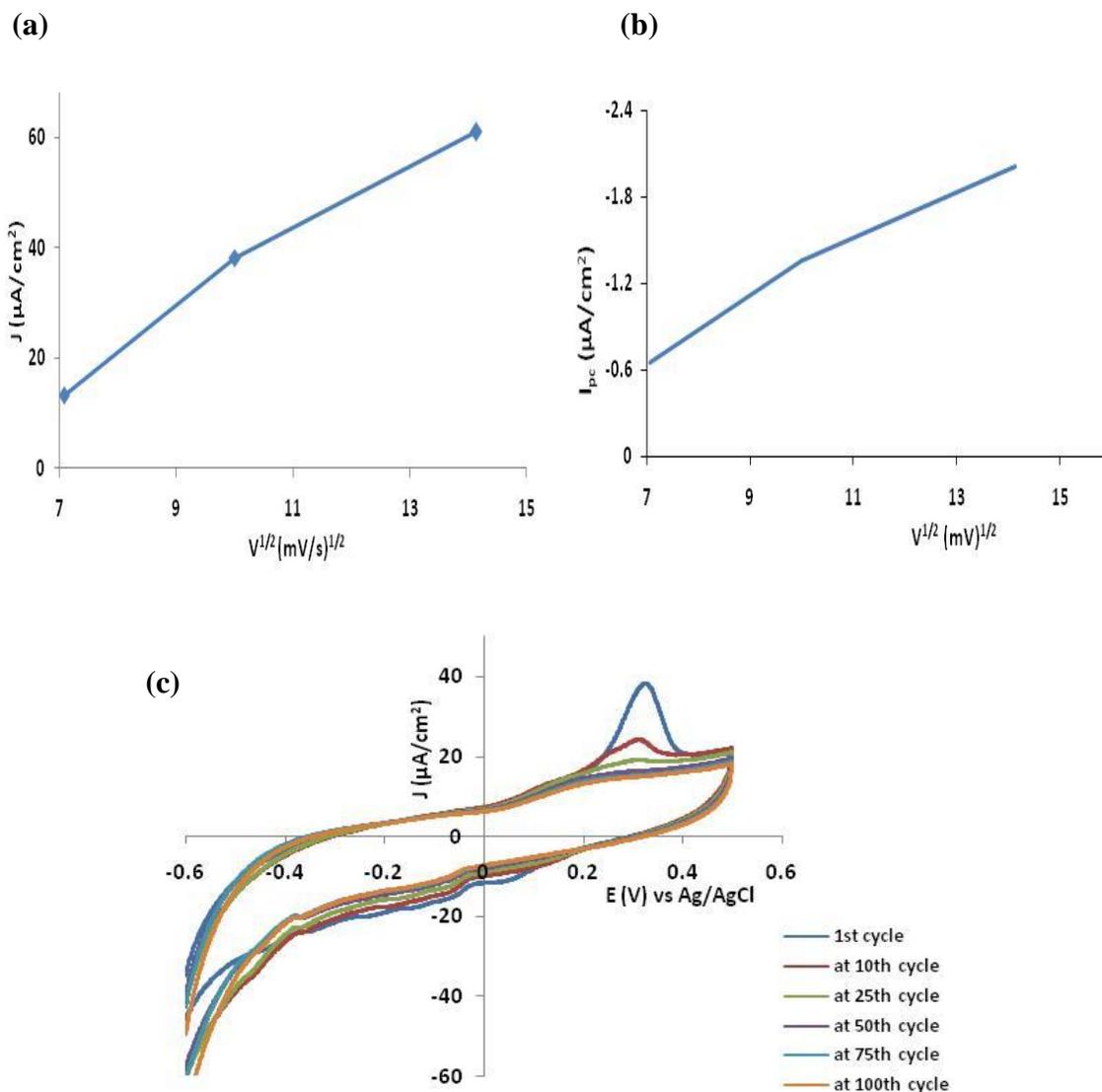


Figure 7: (a) Plot of current density versus square root of scan rates
 (b) Plot of peak cathodic current density versus square root of scan rates and
 (c) Stability of Au-Ag bimetallic catalyst under acidic condition at 100mV/s and room temperature.

The electroactive area of the Au/Ag nanoalloy catalyst is 0.136 cm^2 .

Stability of Au-Ag Nanoalloy Catalyst

In order to evaluate the stability of Au-Ag nanoalloy catalyst, cyclic voltammograms were recorded at 1st, 10th, 25th, 50th, 75th and 100th cycles at a scan rate of 100mV/s (Figure 7c).

The initial peak current density (I_p^*) value of $38.24 \mu\text{A}/\text{cm}^2$ at electrode potential of 0.325V was

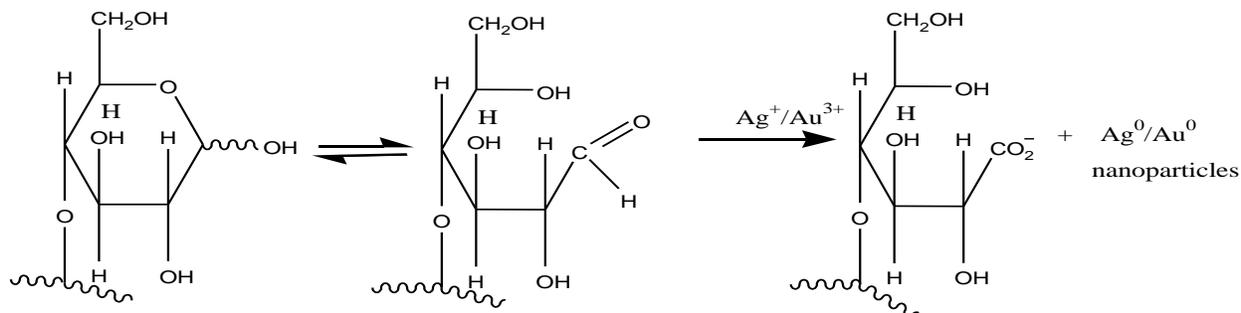
observed at the 1st cycle. At the 10th cycle, I_p^* value decreased to $23.61 \mu\text{A}/\text{cm}^2$ i.e. 61.7% of the initial current density value was left. At the 25th cycle, about 50% of the catalyst activity remained while at the 50th cycle, the I_p value decreased to $16.44 \mu\text{A}/\text{cm}^2$ which translated to 43.0% of the initial I_p^* value. Finally, I_p value of $15.11 \mu\text{A}/\text{cm}^2$ was obtained at the 100th cycle corresponding to 39.5% of the initial I_p^* value.

The gradual decrease in the I_p values at higher cycles might be due to slow decomposition of the catalyst under reaction condition and

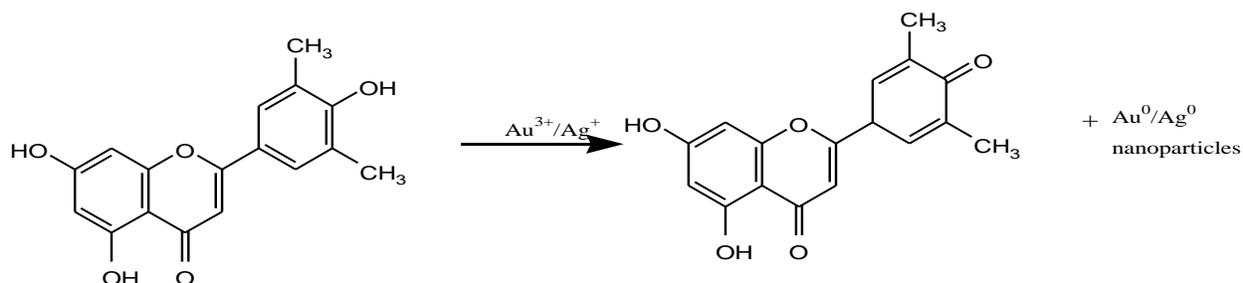
poisoning effect of CO intermediates on the Au/Ag nanoalloy surface. The % stability obtained from this study is lower than those reported with carbon-supported Pt/Ni bimetallic nanoparticles and Au/Pd core-shell catalysts (Tan *et al.*, 2012; Habibi and Dadashpour, 2013).

The bioreduction, capping and stabilisation of the nanoparticles is attributed to these phytochemicals the polyphenols, flavonoids, proteins and carbohydrate in the extract as shown in the proposed mechanisms.

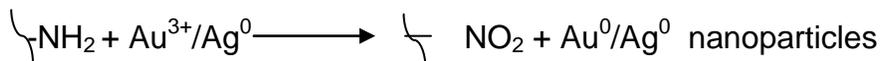
Carbohydrate in the Extract



Flavonoids/Polyphenols



Protein (-NH₂ Group in Amino Acid)



Such roles by flavonoids, terpenoids, proteins and thiamine in plant extracts have been reported in literature (Daisy, 2010; Raut *et al.*, 2013).

CONCLUSION

We have demonstrated the effective use of aqueous extract of *Chrysophyllum albidum* as a reducing agent for the synthesis of Au, Ag and Au-Ag bimetallic nanoparticles or nanoalloys. The optical properties of the nanoparticles showed the characteristic SPR features of the metals. Both the metals and the bimetal heterostructure displayed quasi-spherical morphology. The Au-Ag bimetallic nanoparticles displayed improved activity and stability of the catalyst, catalytic activity with current density value of $38.24\mu\text{A}/\text{cm}^2$ at 0.325V towards the electrooxidation of methanol. The catalytic performance was attributed to the electronic and chemical nature of the Ag metal in the nanoalloy.

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