Biosynthesis, Characterization and Material Applications of Gold, Silver, and Palladium Nanoparticles using Aqueous Extract of *Basella alba* Leaves (Basellaceae).

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ABSTRACT

Gold, silver, and palladium nanoparticles were synthesized using aqueous extract of *Bassella alba* leaves as reducing, capping, and stabilizing agents. Characterization of nanoparticles was carried out using UV-Visible spectroscopy, X-ray diffraction (XRD), and Transmission Electron Microscopy (TEM). All the metal nanoparticles exhibited face centered cubic crystalline structures. TEM images exhibited close spherical morphology with particle size ranges of 20-25 nm, 16-25 nm and 10-14 nm for gold, silver and palladium nanoparticles respectively. A simple, efficient and ecofriendly route of metal nanoparticles was established and basic applications are stressed.

(Keywords: biosynthesis, *B. alba,* metal nanoparticles, TEM, XRD, Basellaceae)

INTRODUCTION

The evolution of nanotechnology had stimulated greater multidisciplinary research in agriculture, science, medicine, and technology. Nanotechnology is mainly associated with the synthesis of nanoparticles of variable sizes, shapes, chemical compositions, and controlled dispersity and their potential use for human benefits (Kumar and Yadav, 2009). The unique optoelectronic, thermal, chemical, mechanical properties, and large surface area of nanoparticles are responsible for their widespread applications. Nanoparticles such as gold, silver, and palladium have found tremendous applications in antimicrobial studies (Emeka *et al*., 2014), pollution control (Huang and Chang, 2006), drug delivery (Emerich and Thanos, 2006), biolabelling (Tkachenko and Feldheim, 2003), and catalysts in various chemical reactions such as Suzuki cross-coupling, Heck and Hiyama reactions (Han *et al*., 2008; Zhang *et al*., 2009).

Conventional synthetic routes for metal nanoparticles include polyol process, electrochemical reduction, and sonochemical (Xiong *et al*., 2005; Cha *et al*., 2007; Nemamcha *et al*., 2006). However, most synthetic routes often involve the use of expensive and toxic chemicals as capping, reducing, and stabilizing agents which contributes to environmental degradation. Green nanotechnology, a combination of nanotechnology and green chemistry, has demonstrated environmentally sustainable methods in the 21st century (Schmidt, 2006).

Research efforts in recent years are directed towards green synthesis involving the use of plants, microorganisms, and biomolecules, which are non-toxic effective reductants, stabilizing agents, and capping agents (Mittal *et al*., 2013). Extracts of *Mangifera indica* and *Cinnamomum camphora*, containing bioactive flavonoids, terpenoids, polyphenols, and carbohydrates have been utilized for green synthesis of metal nanoparticles (Dare *et al*., 2015; Daisy, 2010; Yang *et al*., 2010).

Basella alba (Basellaceae) is a fast growing edible perennial climber, growing up to 9 m in length. *B. alba* extracts possessed antioxidant, antimicrobial anti-inflammatory properties (Kumar *et al*., 2015). Antioxidant activities, total phenolic, flavonoid and ascorbic acid contents of *B. alba* consumed in Nigeria has been reported (Olajire and Azeez, 2011). Nutrients present in *B. alba* include proteins, fat, vitamin A, vitamin E, vitamin

K, and calcium (Roshan *et al*., 2012). Herein, we present for the first time, green synthesis of gold, silver and palladium metal nanoparticles using aqueous extracts *B. alba* leaves.

MATERIALS AND METHODS

Chemicals used in this study were procured from Sigma Aldrich representative in Nigeria.

Collection and Preparation of Plant Materials

Fresh leaves of *B. alba* were collected from a local residence in Ibadan, Nigeria in 2013. *B. alba* leaves were cut into small pieces and washed thoroughly with deionized water and air-dried under shade in the laboratory for 14 days. Finely dried leaves were boiled in deionized water (1:10 w/v) for 20 min. The extract was filtered using a Whatmann filter paper. The filtrate was concentrated *in vacuo* using rotary evaporator and later refrigerated at 4^{o}C.

Biosynthesis of Gold Nanoparticles

4 ml of 0.1 g/mL aqueous filtrate of the extract was reacted with 8 mL of 1 mM gold (III) chloride trihydrate solutions in centrifuge tubes and exposed to microwave irradiation using a DEFY model DMO 35338l microwave at low operating power level 1 for 90 s. The resulting Au nanoparticles were collected by centrifugation using Eppendorf Centrifuge 5702 at 4000 rpm for 5 min and purified by re-suspending in methanol and finally centrifuged at 4000 rpm for 2 min.

Biosynthesis of Silver Nanoparticles

Aqueous filtrate of *B. alba* extract was treated with 1 mM of silver nitrate solution (1: 2; v/v). The resulting solution was heated in a round bottom flask for 20-30 min at 80 ^{o}C. The biosynthesized Ag nanoparticles were collected by centrifugation using Eppendorf Centrifuge 5702 at 4000 rpm for 5 min and purified by resuspending in methanol and finally centrifuged at 4000 rpm for 2 min.

Biosynthesis of Palladium Nanoparticles

Aqueous filtrate of *B. alba* was treated with 1mM palladium (IV) chloride solution and stirred mildly at room temperature. The resulting solution was heated in a round bottom flask for 20-30minutes at 80^{o}C. The biosynthesized Pd nanoparticles were collected by centrifugation using Eppendorf Centrifuge 5702 at 4000 rpm for 5 min and purified by re-suspending in methanol and finally centrifuged at 4000 rpm for 2 min.

Optical Characterization of Metal Nanoparticles

Aliquots of Au, Ag, and Pd colloidal solutions were taken at specific time intervals, bio-reduction of the metal salts to nanoparticles was monitored by measuring the absorbance at 350-800 nm for 20-60 min, in a UV/Visible Varian Cary 50 Spectrophotometer equipped with quartz cuvette (1cm path length).

Characterization of Nanoparticles

Samples for transmission electron microscopy (TEM) analysis were prepared by placing aliquots of Ag, Au, and Pd nanocolloids 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. X-ray diffraction patterns of the nanoparticles were obtained using Bruker D8 Avance X-ray powder diffractometer with Cu Kα (1.5418 Å) radiation.

RESULTS AND DISCUSSION

Optical Properties of Metal Nanoparticles

The optical properties of the biosynthesized metal nanoparticles are shown in Figure 1. Gold and silver metal nanoparticles exhibited distinct surface plasmon resonance (SPR) effect, due to the collective oscillation of free conduction electrons induced by an interacting electromagnetic field (Mulvaney, 1996.). A fine, narrow absorption peak observed at 530–560 nm corresponds to the SPR band of gold nanoparticles, as confirmed by the appearance of a purple colour in the reaction medium (Figure 1b).

Rapid formation of gold 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), the peak intensity increased gradually as a function of reaction time from 10 - 60 min. In the case of silver nanoparticles, SPR absorption band of *B. alba* fell in the range of 330-350 nm, an indication of blue shift in the plasmon band (Figure 1c). The blue shift might be due to the variation in the nature and availability of the biomolecular capping agents (flavonoids, polyphenols, terpenoids, etc.) under the prevailing reaction conditions and is particularly useful and applied in optical materials (Smith *et al*., 2006).

Absorbance intensity which is a function of the concentration of silver nanoparticles increased steadily as the reaction time progressed. A gradual color change from a colorless Ag^{+} solution to deep brown color signaled the formation of silver nanoparticles (Figure 1d). In palladium nanoparticles, a gradual increase in absorbance value was observed from 10-30 min (Figure 1e) indicative of the formation of palladium nanoparticles, confirmed by the disappearance of the absorption peak of Pd^{4+} ions at 430-450 nm within 10 min of reaction and progressive color change from light yellow to dark brown (Figure 1f).

Characterization of Metal Nanoparticles

The XRD patterns of gold, silver and palladium metal nanoparticles (Figure 2) exhibits face centered cubic crystal (fcc) structure. From the X-ray diffraction studies, the nanoparticles exhibited the face centered cubic (fcc) crystal phase. The diffraction peaks for the gold nanoparticles (Figure 2a) were observed at 2θ = 38.48°, 44.63°, 64.98°, 77.86°, 82.16° corresponding to the (111), (200), (220), (311) and (222) facets of cubic gold respectively.

For the silver nanoparticles (Figure 2b), peaks appeared at 2θ values of 38.01° (111), 44.29° (200), 64.04° (220), 77.85° (311). Diffraction peaks for palladium nanoparticles were observed at 2θ = 38.23°, 44.83°, 64.22°, 77.55° and 82.09° corresponding to the (111), (200), (220), (311) and (222) Bragg reflections with the (111) lattice plane as the basal plane (Figure 2c). This is consistent with earlier report on palladium nanoparticles (Sathishkumar *et al*., 2009). The TEM images of metal nanoparticles revealed particles with predominant quasi-spherical morphology (Figures 3a, 3c, and 3e). The particle size ranges were 20-25 nm, 16-25 nm and 10-14 nm for Au and Ag and Pd nanoparticles Figures 3b, 3d and 3f). Alli *et al*., 2011 obtained similar morphology and size range for gold nanoparticles.

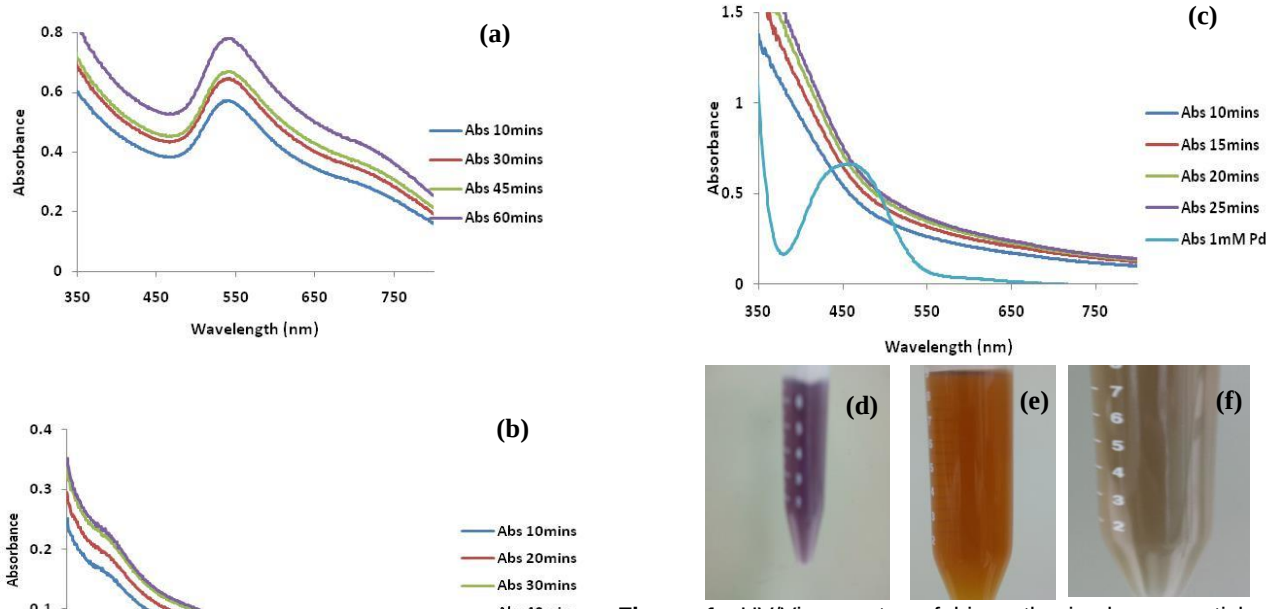


Figure 1: UV/Vis spectra of biosynthesized nanoparticles using 1mM metal salt solution (a) Au nanoparticles, (b) Ag nanoparticles (c) Pd nanoparticles (d) purple colour of Au nanoparticles, (e) brown colour of Ag nanoparticles and (f) dark brown of Pd nanoparticles

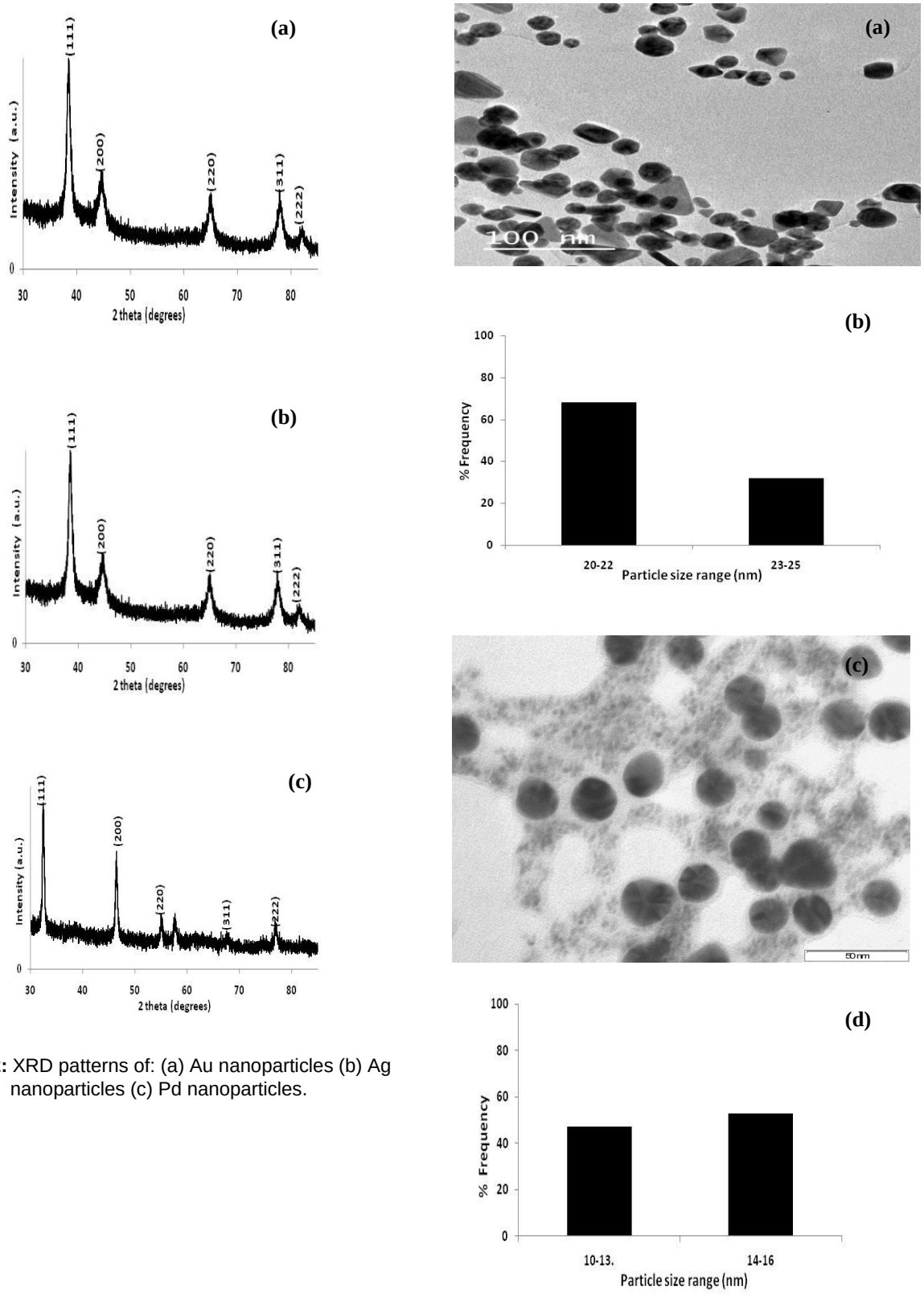
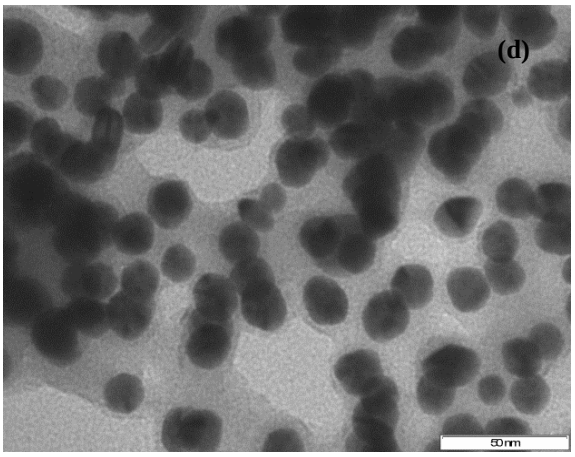


Figure 2: XRD patterns of: (a) Au nanoparticles (b) Ag nanoparticles (c) Pd nanoparticles.



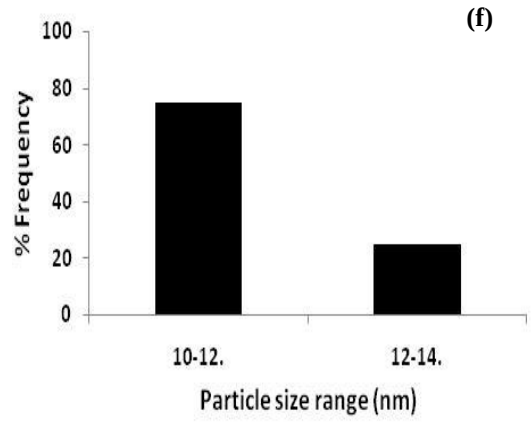


Figure 3: (a) TEM image of biosynthesized Au nanoparticles, (b) corresponding particle size distribution, (c) TEM image of biosynthesized Ag nanoparticles, (d) corresponding particle size distribution, (e) TEM image of biosynthesized Pd nanoparticles, (f) corresponding particle size distribution.

The detailed qualitative phytochemical screening of the aqueous extract of *B. alba* revealed the presence of alkaloids, terpenoids, saponin, cardiac glycosides, flavonoids, carbohydrate, and tannin. It has been elucidated that biomolecules with carbonyl, hydroxyl, and amine functional groups in the carbohydrate, flavonoids, polyphenols and proteins may play important roles in the metal ion reduction, capping and stabilization of the newly formed metal nanoparticles a during their growth processes (Raut *et al*., 2013).

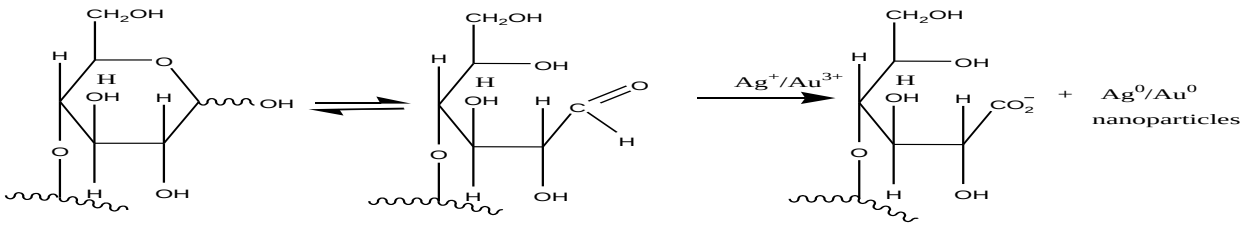
Notable mechanism proposed for carbohydrate and flavonoids are represented thus: Variable roles played by flavonoids, terpenoids, proteins and thiamine in plant extracts have been reported for metal nanoparticles (Daisy, 2010; Raut *et al*., 2013].

CONCLUSION

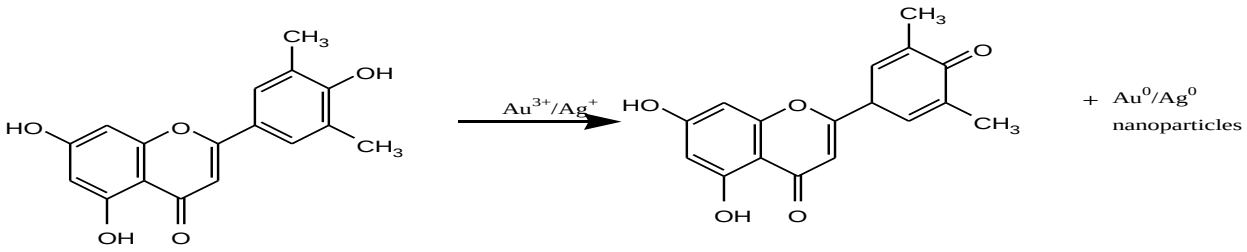
We have utilised an economic and eco-friendly route to synthesize Au, Ag, and Pd nanoparticles using *B. alba* aqueous extract. The optical properties of the nanoparticles showed the characteristic SPR features of the metals. The X-ray diffraction studies of all metal nanoparticles revealed the face centred cubic crystalline phase. The TEM images showed the metal particles with predominantly quasi-spherical morphology.

Notable Mechanism Proposed for Carbohydrate and Flavonoids are Represented Thus:

Carbohydrate in the extract



Flavonoids/Polyphenols



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