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Green Synthesis of Pseudo-Cubic Ag/Ni Bimetallic Nanoparticles using *Senna occidentalis* Leaf Extract

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Abstract.This study reports plant-mediated co-reduction approach for the synthesis of Ag/Ni bimetallic nanoparticles (Ag/Ni BNPs). In view of sustainability development, aqueous leaf extract of an indigenous *Senna occidentalis* (coffee senna) acted as a reducing agent. Cold extraction was carried out on the biodiversity plant using water and methanol as solvent media by way of "green" synthesis. Qualitative analysis was done to identify possible secondary metabolites present in the extract. Synthesis of the nanohybrid was achieved using two different precursor concentrations at 70°C. Techniques including Uv-visible spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy were engaged for optical, morphological and compositional characterisation of the Ag/Ni BNPs, respectively. The reaction colour changed from green to dark brown due to the excitation of electron and change in the electronic energy levels of metal nanoparticles. Presence of nickel in the nanohybrid resulted in blue shift in the absorbance wavelengths when compared with the corresponding monometallic Ag NPs (341 to 327 nm). The optical property displayed by Ag/Ni BNPs is a pointer for potential application as optical material.

Keywords: *Senna occidentalis*, secondary metabolite, optical property, Ag/Ni nanoparticles

1. Introduction

Quest for sustainability development is a demand in science and technology today. Nanotechnology has gained widespread attention in many fields especially inmedicine. Hence, in a bid to safe human health and our environment, there is necessity to focus research on safer synthetic procedures via application of green chemistry which involves renewability, use of non-toxic chemicals, less energy, time saving protocols etc. [1].

Particles with dimension(s) between 1 and 100 nm have been identified to be highly efficient, and of greater performance upon applications in many areas; this is because of unique strength, large surface area, catalytic property, optical activity, strong binding ability among others (physicochemical properties) displayed by the nanoparticles [2-3]. It is worth mentioning that properties of nanoparticles are quite different compared to their bulk materials.

Different methods have been employed by researchers in preparing nanoparticles, these include: chemical, physical and biological procedures [4-5]. Unfortunately, there are disadvantages like intensive energy consumption in physical method which renders the procedure very expensive. Also, use of toxic chemical like sodium borohydride or sodium citrate as reducing agent in chemical method restricts application in clinical fields [6]. Moreover, nanoparticles prepared via chemical route involves use of non-renewable hazardous chemicals as stabilising and reducing agents which pose a threat to human health and environment. Thus, green nanotechnology is considered a way out to overcome the aforementioned challenges. Green synthesis of metal nanoparticles involves the use of organisms, plant extract via phytochemicals like alkaloid, saponins, flavonoid present in them as reducing agents [7]. Plant-based synthesis of nanoparticles has many advantages as the method is considered to be environmentally friendly, cheap and rapid.

Biodiversity plants are recognised for science related research [8]. *Senna occidentalis* (coffee senna) is a sub-tropical, erect, tall (0.8-1.5 m) plant which belongs to the family of Caesalpiniaceae. Its usage comprises liver detoxification, source of oil (seed part), immunity booster etc. [9]. Ethnobotanically, according to Abdillahi and Staden (2013) [10],coffee senna is used in the treatment of infertility and maternal healthcare in South Africa. It is also utilized for its antiparasitic activity in Gabon [11]. Part of Yoruba tribe in Nigeria take the plant in preparing concoction for 7th month pregnancy. Hammad and Suleiman (2015) [12] reported use of *S. occidentalis* (leaf part) in the treatment of malaria and jaundice in Northern Kordofan region of Sudan.

Taking a clue from Prieto*et al*. (2012) [13], bimetallic nanoparticles especially nanoparticles of Ag/Ni are of valuable application as catalysts, electromagnetic wave absorber, electrical contacts, switches and conductor material plating. Recent study revealed application of core-shell Ag/Ni nanoparticles in the hydrogen generation via catalysis [14]. Xiao *et al*. synthesized polyhedral and spherically shaped Ag/Ni bimetallic nanoparticles through laser ablation [15].

Unique optical properties displayed by bimetallic nanoparticles beyond their corresponding monometallic nanoparticles qualify them for application in information technology, sensing etc. [16]. Better electronic and catalytic properties also characterise BNPs which classify them as new emerging nanomaterials. Authors have developed hybrid nanoparticles like silver-gold alloy Au-Ag alloy [17], Pt-Rh nanoparticles using polyol synthesis method [18]. Zheng *et al*. [19] prepared methodical Fe-Pt alloy nanoparticles using direct green solid-phase reduction procedure.

Herein, we report synthesis of Ag/Ni BNPs using plant reduction green method. Biochemicals present in the leaf extract of *S. occidentalis* served as reducing agent instead of harmful chemicals. Optical and morphological analyses of the nanohybrid were carried also out.

2.Experimental

Plant-mediated co-reduction method was used for the Ag/Ni synthesis. Proposed mechanism of the reaction is similar to previous work [20].

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2.1. Materials

S. occidentalis plant was collected in the vicinity of Covenant University, Nigeria. Taxonomical authentication was carried out at Federal Research Institute of Nigeria. Voucher FHI No.109927 was also deposited at the institute herbarium headquarters [21]. Analytically pure $AgNO_3$ and $Ni(NO_3)_2·6H_2O$ were purchased from Sigma-Aldrich company, they were used without additional purification.

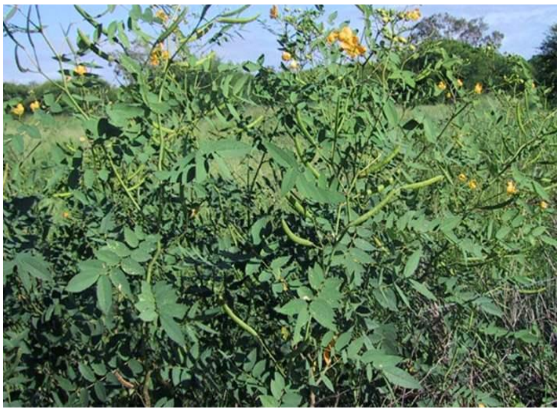


Fig. 1: Image of *S. occidentalis*

2.2. Methods

2.2.1. Preparation and qualitative analysis of S. occidentalis extract

Fresh leaves of coffee senna were rinsed thoroughly with double-distilled water (d-d water) so as to remove impurities. The leaves (25 g) were chopped into pieces with clean blender and extracted with 125 ml d-d water. Mixture was separated using filter paper (Whatman no. 1). Resulting extract was screened qualitatively using standard procedure to identify phytochemicals present [22,23]. The remaining plant extract was reserved in a refrigerator till further use.

2.2.2. Synthesis of Ag/Ni nanoparticles

Ag/Ni bimetallic nanoparticles was prepared by co-reduction method. Two concentrations of precursor solutions- 1.0 and 2.0 mM were prepared separately. To the solution of equal molar concentration mixture of $AgNO_3$ (150 mL) and Ni $(NO_3)_2.6H_2O$ (150 mL) in a beaker, 30 mL of *S. occidentalis* extract was added. The solution was stirred continuously and heated up to 70^0C using magnetic stirrer and hot plate respectively, until noticeable visual colour change was observed in the reaction. Formation and growth of nanoparticles were monitored by taking aliquots of the reaction solution at 10 minutes interval so as to measure absorbance, using Uv-vis spectrophotometer. Isolation of the nanoparticles was achieved by centrifugation method, by means of Thermo Fisher Scientific Centrifuge (Thermo Electron LED), operated at 10,000 rates per minute for 30 minutes. The process was repeated and finally re-dispersed in d-d water, and was centrifuged again. Resulting nanoparticles was dried in an oven at 60^0C before characterisation.

2.2.3. Sample characterisation
Bio-reduction of the equal molar Ag^{+}/Ni^{2+} in the *S. occidentalis* extract was monitored and the optical measurements were recorded on a Genesys 10s Uv-vis spectrophotometer, at 1 nm resolution in the wavelength range between 200 and 800 nm at 25^{0}C. Morphology of the as-prepared nanoparticles was examined with Technai G2 transmission electron microscope (TEM) attached to energy-dispersive X-ray spectrometer (EDX). The equipment functioned at 20 µA current and 200 KeV accelerating voltage.

3. Results and discussion

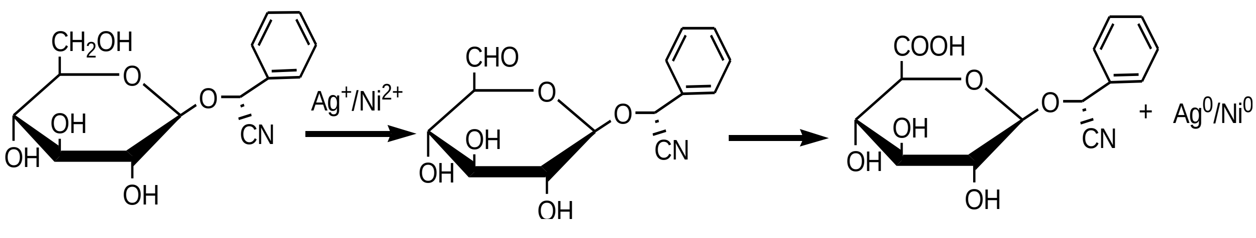
3.1 Qualitative analysis
Results of phytochemical screening of *S. occidentalis* leaf extract is shown in Table 1. Substantial differences were observed in the bioactive agents present in the water and methanolic extracts of coffee senna leaves, as a result of extraction solvents used. Out of the eight biochemicals investigated, glycosides and carbohydrates were noticed in the water extract while additional groups namely, tannins, phenols, flavonoids and alkaloids were detected in the methanolic extract of the same plant; probably these additional groups were more methanol soluble, and the reason for not detecting them in the pure water solvents. Proposed mechanism of the reduction reaction is revealed in Schemes 1 and 2.

Table 1: Qualitative analysis of *Senna occidentalis*leaf extract

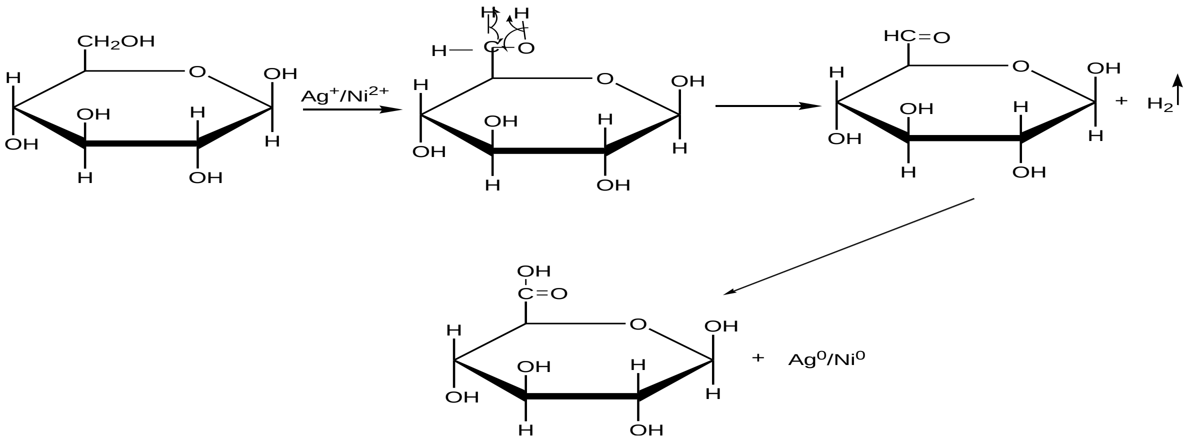
	Senna occidentalis	
Phytochemicals	**Water extract**	**Methanolic extract**
Tannins	-	+
Phenols	-	+
Flavonoids	-	+++
Saponins	-	-
Glycosides	++	+++
Anthraquinones	-	-
Alkaloids	-	+
carbohydrates	++	+++

(+) = Weak; (++) = Strong; (-) = Absence

Proposed mechanism of reaction is shown below in Schemes 1 and 2.



Scheme 1: Bioreduction of silver/nickel ionsto silver/nickel nanoparticles by glycosides [20]



Scheme 2: Bioreduction of silver/nickel ionsto silver/nickel nanoparticles by carbohydrates

3.2. *Optical analysis*

Onset of nucleation and growth started so rapidly, as fast as 2 minutes of the reaction. The reaction colour changed from green to dark brown due to the excitation of electron and change in the electronic energy levels of metal NPs, which informed formation of nanoparticles. This also indicated that the bio-active components (Table 1) present in the *S. occidentalis* leaf extract which was responsible for the reduction of metal ions were adequate.

Optical characterisation was achieved by absorption spectroscopy technique. Absorbance of the nanohybrid was measured, and the Ag/Ni nanoparticles exhibited localised surface plasmon resonance as a result of induction of coherent oscillation of electrons during interaction of electromagnetic field with conduction band electrons in the metal [24]. Surface plasmon resonance band (SPRB) occurred at 327 and 330 nm in 1.0 and 2.0 mM solutions respectively. Higher absorption intensity was attained in the reduced 2.0 mM precursor. Fig. 2 is the absorption spectra of Ag/Ni nanoparticles at 10 minutes intervals. Narrow SPR band was observed in the absorption spectra at 1.0 mM concentration, unlike broad band observed at higher concentration which could plausibly be as a result of anisotropic growth which led to large particle formation. The broad band also connotes aggregation of nuclei and irregular shape according to Kamyshny*et al.* (2010) [25].

Existence of Ni in the hybrid nanoparticles formation resulted in blue shifted absorbance wavelength compared with the corresponding monometallic Ag NPs (341 to 327 nm) in 1.0 mM precursor solution from previous work [21]. The appearance of SPR below 400 nm suggests that the surface of the as-prepared nanohybrid may be enriched by both Co and Ni.

The noticed broad band around 330 nm when 2.0 mM precursor solution was reduced proposes that the surface of bimetallic nanoparticles is highly augmented by Ni, and this is corroborated by the TEM images (Figs. 3a and 4). The hypochromic shift in the absorbance wavelength proposes an application for medical purpose.

Considering redox reaction that took place during Ag/Ni nanohybrid formation, Ag^+ got reduced preferentially due to its higher reduction potential compared with Ni^{2+} as shown in the redox reaction (Eq. 1-5).

$$AgNO_3 \rightarrow Ag^+ + \; NO_3^- \tag{1}$$

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$NiNO_3 \rightarrow +Ni^{2+} + \; NO_3^-$ (2)

$Ag^+{}_{(aq)} + e^- \; \rightarrow Ag^0{}_{(s)}$ $\quad (E_{reduction} \;\; = + \, 0.80 \text{ V})$ (3)

$Ni^{2+}{}_{(aq)} + 2e^- \;\rightarrow Ni^0{}_{(s)}$ $\quad (E_{reduction} \;\; = - \, 0.258 \text{ V})$ (4)

Overall equation: $Ag^+ \; + Ni \rightarrow Ag^0 \; + \; Ni^{2+}$ (5)

Literature shows that when particle size is bigger than 6 nm, decrease in the SPR absorption intensity and broad peak are inevitable due to increase in the concentration of Ni which is noticeable in Fig. 2 [26]. This also suggests that the surface of the nanohybrid is nickel enriched, unlike monometallic Ag nanoparticles which appears around 400 nm in previous studies [27-29].

Morphological feature of the bio-synthesised nanoparticles Ag/Ni bimetallic nanoparticles deposited on a copper grid is depicted in Fig. 3. Broad size distribution of the nanoparticles range between 3 – 24 nm with a mean size of 10.25 ± 4.19 nm (Fig. 3a). The particles are pseudo cubic with little aggregation of nuclei. Nickel rich surface in the TEM micrograph corroborates the observed Uv-vis absorption spectra in the absorbance region less than 400 nm [30]. This is in agreement with elemental composition of the nanohybrid analysed by EDX (Fig. 5).

Synthesis of the bimetallic nanoparticles is supported by the result of EDX analysis (Fig. 5). Elemental analysis showed that silver and nickel were present approximately in the ratio 3:1. Oxygen and carbon were present with the atomic composition of 5.44% and 10.47% respectively, and this signified the presence of organic capping agent provided by the phytochemicals for stability.

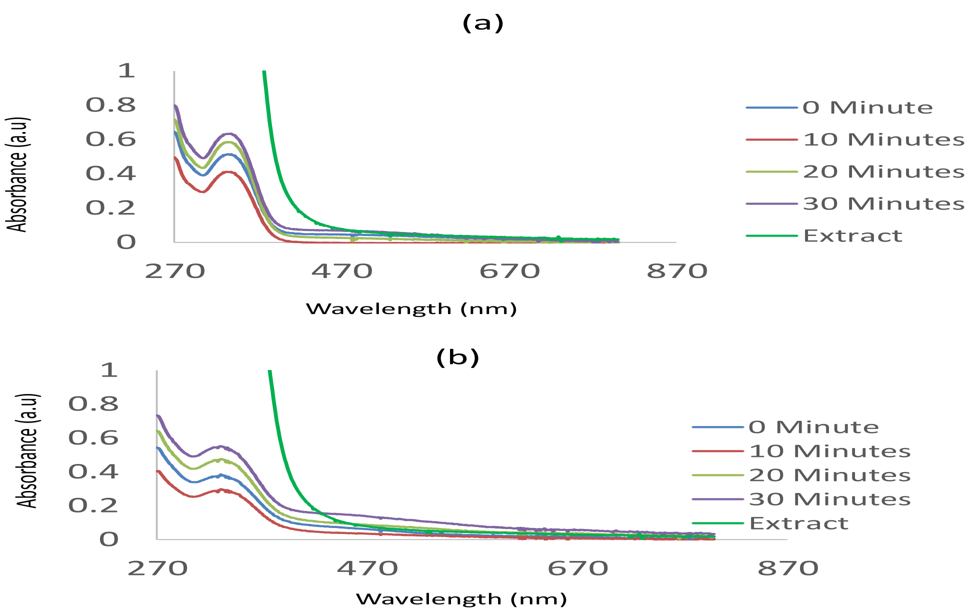

Fig. 2: Uv–vis absorption spectra of Ag/Ni nanoparticles reduced with: (a) 1.0 mM (b) 2.0 mM solutions at 70^{0}C

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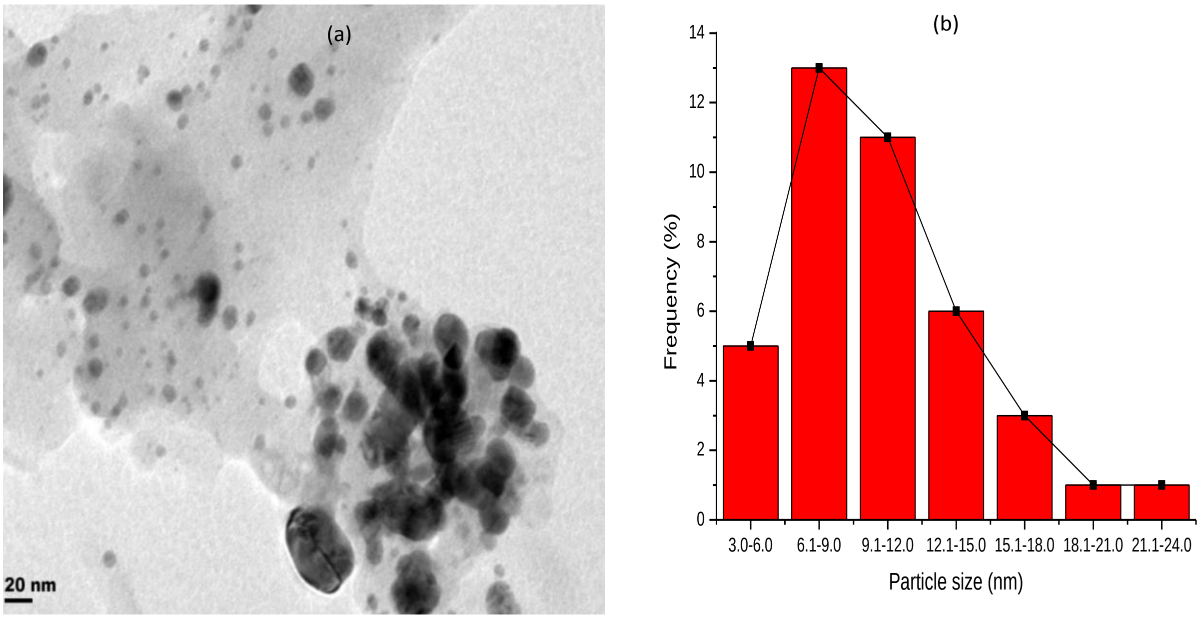

Fig. 3: (a) TEM image of Ag/Ni bimetallic plant-based synthesis (b) Histogram of particle size distribution

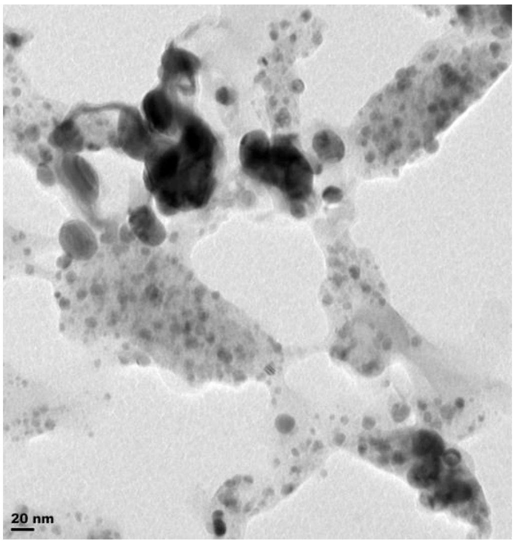

Fig. 4: Representative TEM images of Ag/Ni bimetallic nanoparticles

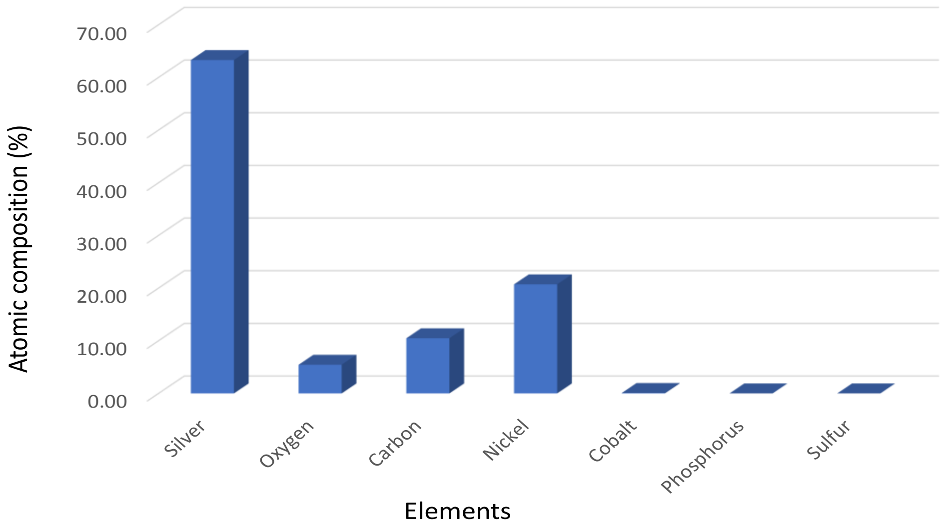

Fig. 5: EDX of Ag/Ni bimetallic nanoparticles

4. Conclusion

Synthesis of bimetallic Ag/Ni nanoparticles by green reduction method was successful. The nanoparticle surface is enriched in Ni as showed in the absorbance wavelength (330 nm). TEM images showed that the nanohybrid possess pseudo-cubic morphology, supported by the elemental composition revealed in the EDX analysis. No doubt, the nanoparticles possess optical activity as displayed in the Uv-vis absorption spectra, and the hypochromic shift in the absorbance wavelength proposes an application for medical purpose.

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Conflict of interest

No conflict is declared.

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