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THE DESIGN AND CHARACTERIZATION OF MODIFIED POLYTHIOPHENE SUPPORTED PLANT MEDIATED CO-NI BIMETALLIC NANOCOMPOSITES

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ABSTRACT

Ficus mucuso leaf extract was employed as reducing agent in the synthesis of Co-Ni bimetallic nanoparticles (BMNPs) with two precursors namely; Cobalt (ii) nitrate hexahydrate; [CO(NO3)2.6H2O] and nickel (ii) nitrate hexahydrate; [Ni (NO3)2.6H2O]. Afterwards, acid modified polythiophene was synthesized through the in-situ and ex-situ coupling approach. The nanocomposite obtained from the in-situ method was labelled 'A' and that of the ex-situ, 'B'. The in-situ approach was considered to be more appropriate for synthesizing the BMNPs as confirmed by characterization using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray diffraction analysis (XRD), Energy dispersive X-ray (EDX) analysis, Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA) and Scanning electron microscopy (SEM) techniques. The hexagonal cobalt and the cubic nickel were investigated using XRD to determine the particle sizes taking Debye-Scherrer's equation to be around 14.495nm for sample A and 15.689nm for sample B. This was reported to be responsible for the corresponding intense peak at A over B. The SEM and TEM measurements portray good correlation indicating the presence of agglomerates in sample B. The EDS analysis taken reported a higher weight of the cobalt and nickel compositions in A than in B. TGA explained the higher decomposition rate of B than A. Also, a more pronounced intense peak was observed in A than in B using FTIR technique. This comparison of both samples makes in-situ synthesis unquestionably the best because of its outstanding performance over ex-situ approach. This is the first report of *Ficus Mucuso* plant extract being used in nanosynthesis.

Keywords: Co-Ni Bimetallic Nanoparticles, In-situ, Ex-situ, Polythiophene

INTRODUCTION

Materials science is replete with researchers' exploration and application of nanoparticles, although the concept really expanded during the industrial revolution [1]. The concept entails a framework whose size is higher than sub-atomic measurements and lower than naturally visible ones (i.e.> 1nm and < 100nm) [2]. Nanomaterials have been widely used in various fields due to their electrical, magnetic, optical and chemical properties. They have found expression in wastewater treatment, catalysts, modern industries, sensors and biosensors, electrodes for

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batteries and capacitors, dye industries, and microwave devices. These materials have been greatly used in different fields of life such as medicine, civil engineering, bioanalysis, physics, agriculture and food. [3]

Several nanocomposites such as metal matrix nanocomposite [4], ceramic nanocomposite [5], and polymer nanocomposite [6] have been designed by researchers while Polymer nanocomposites have specifically been proven to be synthesized via in-situ formation and sol-gel [7-8], in-situ intercalative polymerization [9], ex-situ polymerization [10-11], solution mixing [12] etc. Polymer metal nanocomposites are useful for many technological applications especially in advanced functional materials such as sensors, hydrogen storage system, polarizers, microwave absorbers, optical limiters and high energy radiation shielding materials.

In this research, Polythiophene (PT) was used with its novel properties made possible from the combination of nanostructured PT and other nanomaterials such as metal oxide and conducting metals (Co, Ni, Au, Pt, etc.) [13]. They can be prepared using two different approaches which include in-situ and ex-situ techniques. In-situ method involves the generation of metallic nanoparticles inside a polymer matrix by decomposition through processes like photolysis, thermolysis, radiolysis etc. or by the chemical reduction of a metallic precursor present in the polymer. The ex-situ method on the other hand involves the production of nanoparticles firstly by some soft chemistry means and then dispersing into the polymer matrix [11]. The advantage of in-situ over ex-situ method is that it prevents particle agglomeration in order to keep good spatial distribution in the polymer matrix. As a result of the in-situ technological advances, this approach has been the major focus of great attention and application.

Again, synthesis of metallic nanoparticles could either be of the monometallic, bimetallic, trimetallic and more, based on the number of metallic ingredients of the precursor salts [14]. Bimetallic nanoparticles (BMNPs) have been found to have some mixing pattern characteristics and geometrical architecture which increases their functionality as they show better catalytic activity, stability, and selectivity over monometallic particles. These characteristics of BMNPs are due to the presence of two metals which each plays a particular function to carry out the overall mechanism of reaction [15]. Previously, many BMNPs have been used by researchers. For example, Cu-Ag BMNPs was synthesized for its antibacterial and catalytic activity areas [16], Fe-Cu BMNps was synthesized using *Ficus* leaves for removing orange dye from aqueous medium [17], bimetallic oxide nanohybrids was also synthesized for the removal of selenium in water [18].

Synthesis of cobalt and/or nickel nanoparticles has been carried out using sol-gel method [19-20], hydrothermal method [21-23], microemulsion method [24], solvothermal method [25-26],

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ultrasonic method, [27-29], electrochemical method [30-31] micro-electrical method [22] and plant-based method [32-36]. But none of these aforementioned methods of synthesizing bimetallic nanoparticles involved nickel and cobalt. Therefore, Co-Ni BMNps via green synthesis using *Ficus mucuso* as reducing agent with the aid of [CO(NO3)2.6H2O] and [Ni (NO3)2.6H2O] was designed. The choice of genus *Ficus* from the family of the Moraceae, made up of some important plant metabolites such as flavonoids, tannins, and phenolics (crucial in producing *Ficus*-zero valent cobalt or nickel nanoparticles) is because of their lack of negative effect [37]. Also, many *Ficus* plant species have been found to be ecofriendly, biodegradable, economical, and acting as capping as well as reducing agent [17]. However, this is the first time the plant *Ficus mucuso* is being used in nanosynthesis. This study reported the characterization of the synthesized BMNCs via different characterization techniques.

MATERIALS AND METHODS

Preparation of aqueous leaf extract of Ficus mucuso

Ficus mucuso leaves were collected from Forestry Research Institute of Nigeria, Ibadan, Oyo State. It was further identified at the herbarium at the Department of Plant Biology, University of Ilorin, Kwara State and given a voucher number UILH/001/1657/2023. The leaves were rinsed thoroughly with distilled water to remove impurities, dried at room temperature, and later grounded into powder. 10g of it was measured into the conical flask and 50 ml ethanol with 50ml of distilled water was added and stirred on a magnetic hot plate at 60°C for 1 hour. The mixture was made to cool and then filtered with Buchner funnel and membrane filter system

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connected to a vacuum pump. The filtrate was later kept sealed with an aluminum foil.

In-situ and ex-situ preparation of functionalized polythiophene supported Co-Ni BMNps using Ficus mucuso extract

The bimetallic nanoparticles (Co-Ni) were synthesized by taking 40 ml of the filtrate collected during extraction and adding 0.116g of cobalt (II) nitrate hexahydrate (Co precursor) and 0.116g of nickel (II) hexahydrate (Ni precursor). The mixture was stirred for 15 mins and 0.012 g of maleic anhydride with 0.116g of polythiophene was added and stirred for 8 hours on the magnetic hot plate at 120°C which is the in-situ process. The ex-situ synthesis was also carried out by separately synthesizing Co-Ni BMNps followed by functionalization of polythiophene with maleic anhydride under the same condition of temperature and time. The prepared Co-Ni bimetallic nanocomposite and functionalized polythiophene were then blended in 50 mL of 1:2 ethanol and DMSO solvent mixtures. The powdered products obtained from in-situ and ex-situ were coded as samples A and B respectively, and then kept for analysis in sealed glass vials at room temperature.

Characterization of the in-situ and ex-situ PT/Co-Ni bimetallic nanocomposites

The morphological properties of the BMNCs were investigated using Scanning Electron Microscopy (JEOL, JSM-6060 SEM) and the elemental component and distribution were determined with an Energy Dispersive X-ray Spectroscopy (EDS) [38]. The functional group of the nanocomposites on their different surfaces were discovered by Fourier Transform Infrared Spectroscopy (Shimadzu FTIR-8400S, Japan) to investigate the absorption band with a wavelength ranging from 4000 to 500cm-1 at 8cm-1 resolution. The transmission electron microscopy (TEM) images of nanoparticles were obtained with a JEOL sputter ion coater and then observed at 15 kV at magnifications (×500 transmission electron microscope) operating at 120 kV [39]. The nanocomposites crystallinity (crystal structure; which reveals the order of arrangement of different atoms involved) and phase purity of the synthesized BMNCs [40] were investigated using X-Ray Diffractometer (XRD Pan Analytical), which works with Cu Kα emission at a scanning rate of 2Θ angles/min at 45Kv and 40mA per sec, the crystallite size was calculated using Debye–Scherrer equation:

$$D = {}^{K\lambda}/_{\beta cos\theta}$$

Where $\beta =$ FWHM (Full-width at half maximum or half width) is the line broadening at FWHM in radians; Θ is the Bragg's angle in degree (half of 2Θ); K is the Scherrer constant which is equal to 0.94; λ is the X-ray wavelength = 1.5406 Å**.** Also, d-spacing (interplanar distance) from the XRD spectra was taken using Bragg's equation;

$$d = {}^{n\lambda}/_{2\sin\theta}$$

Where d is the d-spacing or interplanar distance, λ is the X-ray wavelength = 0.15418nm, n is the order of reflection = 1,2,3 etc. and Θ is the Bragg's angle in radian.

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RESULTS AND DISCUSSION

Material characterization

The XRD patterns of A and B confirm that cobalt-nickel bimetallic NPs are successfully formed. All diffraction peaks were indexed to the hexagonal cobalt crystalline phase (Space group: P63/mmc) and as well to the cubic nickel crystalline phase (Space group: Fm3m). The crystallite size was estimated to be 14.495 nm and 15.689 nm for samples A and B. It was observed that the crystallite size of B which was prepared ex-situ was higher than that of A which was prepared in-situ. This implies that the nucleation and growth kinetics of A was ordered unlike B with random or chaotic nucleation. The XRD pattern corresponding to four intense diffraction peaks which is indexed at 22.64, 32.21, 51.95 and 57.34.

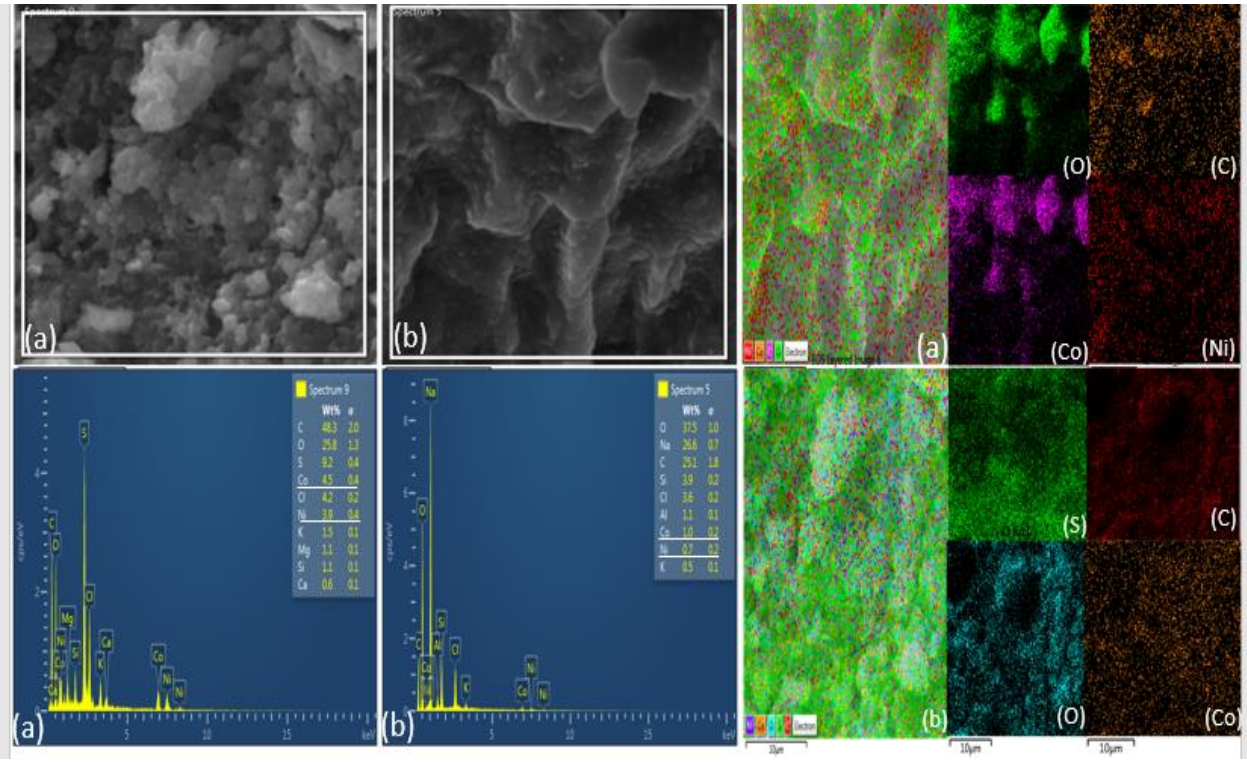

Fig 1 Morphological studies (SEM and EDX) images of the BMNCs

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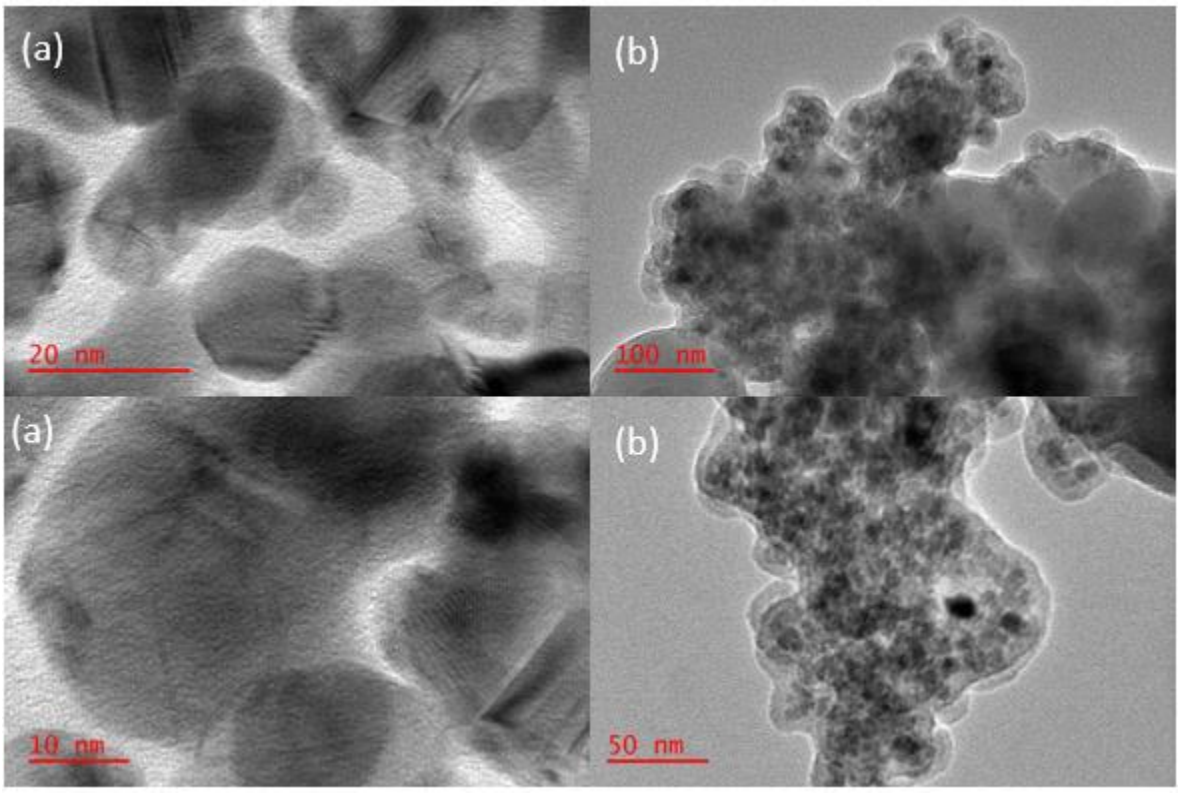

Fig 2 TEM images of the BMNCs

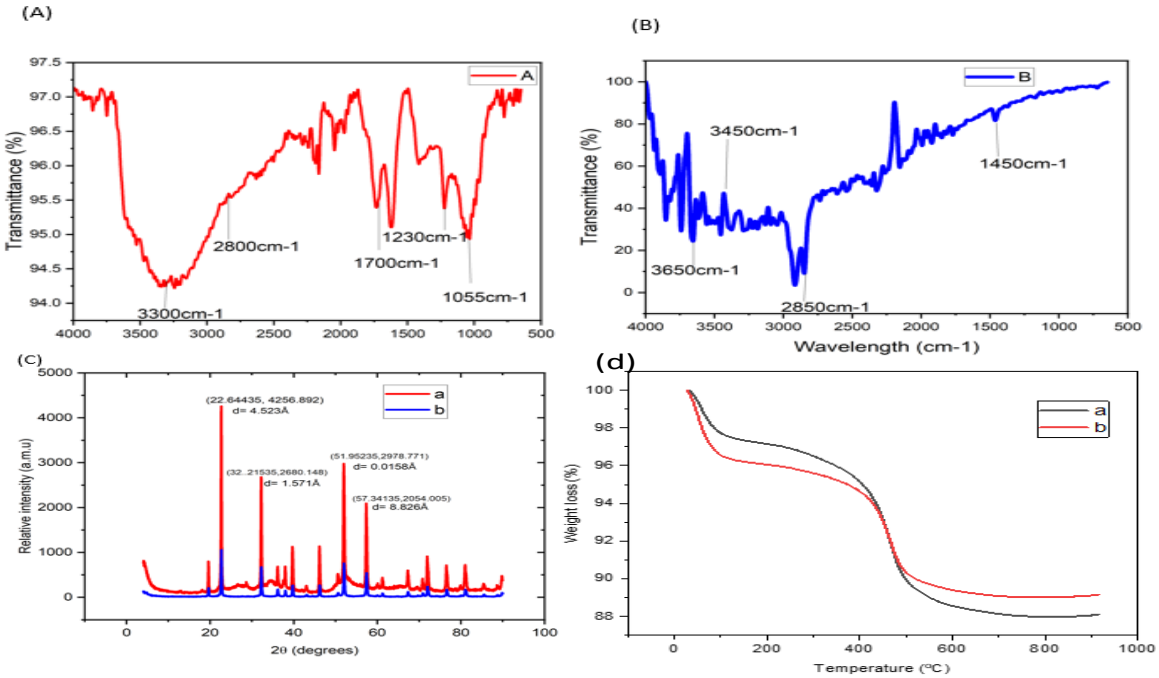

Fig 3 FTIR, XRD and TGA of the Co-Ni BMNCs

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The FTIR spectra of the BMNCs is shown in figure 3a and b. Spectrum A showed a strong and broad band at 3300cm-1 which is attributed to the hydroxyl group, the band at 2800cm-1 can be assigned to aldehyde C-H stretching, the band at 1700cm-1 refers to C=O stretching of the carbonyl group, and the bands at 1230cm-1 and 1055cm-1 also correspond to a C-O stretch of a phenol and alcohol group, to respectively. Spectrum B on the other hand, has band at 3650cm-1 indicating the -OH hydroxyl group stretching, and a dimeric -OH stretch at 3450cm-1 with a -CH stretch of an alkane at 2850cm-1 in addition to the O-H bending of the carboxylic acid corresponding to 1450cm-1. In the FTIR spectra of the BMNCs, the IR bands correspond to hydroxyl, aldehyde, carbonyl, phenol, alcohol, alkane and carboxylic acid groups. The chemical composition of Ficus mucuso is responsible for the reduction of the salts [CO(NO3)2.6H2O] and [Ni (NO3)2.6H2O] into their respective nanoparticles. The availability of the secondary plant metabolites such as flavonoids, phenolics, tannins etc. in the plant is attributed to its capping or reduction action [17].

The morphology of the bimetallic nanocomposite was determined by SEM analysis conducted on both composites [41] as shown in figure 1. Sample A, has an invisible polythiophene bed covered by the BMNPs. It was observed to possess irregular structures, macrospore and some of them bonded together as Ficus mucuso. Sample B on the other hand, revealed formation of large agglomeration and clusters at 10μm of Co-Ni as a result of the large amount of heat reacted on the sample which caused the formation of polythiophene beds which appear as ridge-like forms hosting well-packed Co-Ni BMNPs. The elemental mapping for the samples revealed some elements like carbon, oxygen, cobalt and nickel in A. While sample B contains elements such as oxygen, sulphur and carbon. Other elements present in both samples are likely some constituents in the polythiophene used for the synthesis. The report from the EDX measurement revealed that sample A which was conducted in-situ contains a higher percentage of Co and Ni (4.5 and 3.9% respectively) than B which was conducted ex-situ with weight percentage of Co and Ni of 1.0 and 0.7%, respectively. The low percentage weight in B is as a result of the high decomposition level of the ex-situ process.

Transmission electron microscopy technique was conducted to visualize the morphology of the nanocomposites for A and B. Sample A showed a flat and spherical-like shape of the polythiophene which was embedded in-situ in the BMNPs. Sample B showed an agglomeration of the polythiophene which was embedded ex-situ in the BMNPs. The sizes of the different TEM images range from 10-20nm for sample A and 50-100nm for sample B. The TEM images also revealed the functionality of polythiophene on the nanomaterial. As observed in A, lack of agglomeration due to the presence of the polymer (polythiophene) supports the nanomaterial, accounting for its high functionality, lacking in the counterpart.

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Co-Ni BMNPs embedded in polythiophene was investigated using thermal gravimetric analysis and the mass of the BMNCs was measured over time. This was to determine the amount of organic molecule residue in the nanoparticles during decomposition and to investigate their properties. Figure 3 shows that Co-Ni starts to decompose at 1000c where 3% and 4% of sample A and B were lost respectively. The Co and Ni precursors used experienced the major weight loss at 5000c. The decomposition of nanoparticles in B was very fast unlike in A, which took place gradually and continued decomposing until it finally turned to ash. It was evident that the thermal decomposition of B was quick due to its ex-situ method of synthesis while that of A was slow because of its in-situ method of synthesis.

CONCLUSION

Substantial progress has been made in the biosynthesis of Co-Ni bimetallic nanoparticles using plant extract for important applications by embedding it on a polymer matrix. But this research used Polythiophene owing to its special photovoltaic property as well as its high environmental stability and conductivity. Several facile approaches are utilized to give nanocomposites with special characteristics like spherical and flat nanocrystals (with appropriate compositions, shapes and particle sizes) magnetic properties and enhanced synergistic ability. Such approaches include the in-situ and ex-situ synthesis of the polymer nanocomposites. The results from investigation of both approaches were reported from the various results of characterization measurements such as structural, morphological, XRD, FTIR and TGA (Thermal decomposition). It was concluded that the in-situ method is superior in the synthesis of Co-Ni BMNCs compared to the ex-situ method owing to its lack of agglomeration. This property helps to keep good spatial distribution of the polymer matrix.

Although transition nanoparticles (such as cobalt and nickel) exhibit excellent properties and applications, more toxicological research is expected in order to eradicate any adverse effect that there may be. Finally, it should be noted that the aspect of in-situ synthesis method requires more researches to prove its superiority over the ex-situ method.

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