



MOPHOLOGY OF POLYANILINE NANOTUBE WITH VARIOUS LEVEL OF Fe₃O₄ NANOPARTICLES AND THEIR ELECTRICAL CONDUCTIVITIES BY ULTRASONIC DISPERSION METHOD

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ABSTRACT

The conductivities of the obtained PANi/Fe₃O₄ composite nanotubes prepared by ultrasonic dispersion method were measured by the standard Van Der Pauw DC four-probe method. Conductivities of the composites were measured as a function of wt% Fe₃O₄ nanoparticles. It was found that the conductivities of the PANi nanotubes containing different wt% Fe₃O₄ nanoparticles are lower than that of bulk PANi and decreases with the increase of wt% Fe₃O₄ nanoparticles. The conductivities also increase as the doping level in the composite increases. The FTIR Spectra indicate the presence of PANi containing Fe₃O₄, FESEM results prove that nanostructure of PANi/Fe₃O₄ is produced by this method. The lower conductivities of PANi/Fe₃O₄ composite may be due to the lower concentration of dopant used in the polymerization process and the optimization of this composite allows this material being use as a matrix for development of electrochemical sensors.

Keywords: polyaniline, nanocomposites, conductivity, Fe₃O₄.

1. INTRODUCTION

Polyaniline (PANi) nanostructures have been prepared by blending PANi with inorganic electrical, optical, and magnetic nanoparticles to form nanocomposites (Lu *et al.*, 2004; Lu *et al.*, 2005). Among the inorganic nanoparticles, Fe₃O₄ nanoparticles have received great attention because of their interesting magnetic properties as well as extensive potential applications in color imaging, magnetic recording media, soft magnetic materials and ferrofluids (Lu *et al.*, 2006). There are also significant researches devoted to the design of metal nanoparticle-conducting polymer composite based biosensors (Feng *et al.*, 2006 & Yan *et al.*, 2008).

The properties of conducting polymers as sensing materials can be improved by the preparation of conducting polymer-based composites. For examples, the intercalation of conducting polymer in layered host inorganic materials and other structurally organized environments resulted in organic/inorganic hybrid nanocomposites (Xia *et al.*, 2010). Other example includes sensors based on conducting polymer/inorganic semiconductor composites (Joshi *et al.*, 2008), conducting polymer/piezomaterials (Patil *et al.*, 2007) and conducting polymer/biomolecule composites in sensing applications (Xia *et al.*, 2010). These hybrid nanomaterials are expected to display synergistic properties between the polymer and the metal nanoparticles (Yan *et al.*, 2008). Their novel electrical, structural and mechanical properties make them excellent candidates as sensing materials (Xia *et al.*, 2010).

Fe₃O₄@Au/polyaniline (PANi) nanocomposites were fabricated by *in situ* polymerization in the presence of mercaptocarboxylic acid (Yu *et al.*, 2008). Recently, PANi/Fe₃O₄ nanocomposite has become a popular material for applications in electrical-magnetic shields,

electrochemical display devices and microwave absorbing materials. There are many methods to produce PANi/Fe₃O₄ nanocomposite (Lu, *et al.*, 2005). The most general method is by direct polymerization of aniline monomers in an aqueous solution in the presence of dispersed iron oxide particles (Lu, *et al.*, 2005). Other methods include (1) blending the PANi in N-methyl-2-pyrrolidone (NMP) with iron (II) sulfate aqueous solution and precipitating Fe²⁺ into maghemite, and (2) allowing the monomer to react with FeCl₂·4H₂O and FeCl₃·6H₂O, followed by treatment with aqueous KOH (Lu, *et al.*, 2005).

Deng *et al.*, reported the preparation of PANi-Fe₃O₄ nanoparticles with core-shell structure via an *in situ* polymerization of aniline monomer in an aqueous solution, which contains Fe₃O₄ nanoparticles and surfactant NaDS (Deng *et al.*, 2003). Most of these methods require vigorous stirring of the solution to suspend the magnetic particles and prevent the aggregation of the nanosize magnetic particles during the reaction (Lu *et al.*, 2005).

The functionalization of inorganic components by PANi was found to improve the colloidal stability and the nature of association between the components (Ahmad, 2013). The synthesis techniques, characteristics and loading amount of inorganic materials influenced the ultimate properties of the composite (Ahmad, 2013).

In this study, the PANi/ Fe₃O₄ was synthesized using a simple technique that allows the synthesis of PANi/ Fe₃O₄ nanotubes by ultrasonic of aqueous solutions of aniline, ammonium peroxydisulfate (APS), phosphate acid, and the quantitative amount of aniline dimer-COOH capped Fe₃O₄ nanoparticles (Lu, *et al.*, 2006). The obtained sample have the morphology of a nanotube,



dopant (H_3PO_4) and (Fe_3O_4) nanoparticle level affects the conductivity of the nanocomposites.

2. EXPERIMENTAL

a) Materials

Aniline monomer was distilled under reduced pressure and stored below 0 °C. All the other reagents were analytical grade, and used without further purification, including Ammonium peroxydisulfate (APS), Phosphoric acid (H_3PO_4), N-phenyl-1,4-phenylenediamine, Succinic anhydride, Diethyl ether, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NH}_3 \cdot \text{H}_2\text{O}$, HCl, CH_2Cl_2 and Methanol.

b) Synthesis of Aniline dimer-COOH

The reaction was carried out in a 100-mL three necked round bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet. N-phenyl-1,4-phenylenediamine 0.921 g (5.0mmol) and succinic anhydride 0.500 g (5.0mmol) were dissolved in 30mL CH_2Cl_2 with stirring at room temperature for 5 h. As the reaction proceeded, white-grey precipitate was formed. At the end of reaction, the precipitate was collected by filtration and washed with diethyl ether until the filtrate became colourless. The product was dried under vacuum for 12 h at room temperature.

c) Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared as described by (Lu *et al.*, 2005): 0.86 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved under N_2 in distilled deionized water (20mL) under vigorous stirring. As the solution is being heated to 60 °C, $\text{NH}_3 \cdot \text{H}_2\text{O}$ (28% (w/w), 5mL) was added, quickly followed by addition of a solution of aniline dimer-COOH (200 mg) in 2mL of acetone. The reaction was allowed to proceed for 1 h at 80 °C with constant and vigorous stirring to produce a stable, water-based suspension. The reaction mixture was then cooled slowly to room temperature. The suspension was washed sequentially with acetone and ethanol.

d) Preparation of PAni- Fe_3O_4 composites

PAni- Fe_3O_4 composites were synthesized by ultrasonic irradiation method. In a typical procedure, 0.2mL aniline monomer were mixed with H_3PO_4 (0.05mL) and 5 wt % Fe_3O_4 dissolved in 15mL of deionized water under ultrasonic stirring for 10min to form an emulsion of aniline/ H_3PO_4 complex containing Fe_3O_4 nanoparticles at room temperature. The reaction was repeated varying the amount of both the dopants (H_3PO_4) and Fe_3O_4 . Then 5mL aqueous solution of APS (0.46g) was added to the above mixture. The reaction was kept by ultrasonic stirring for 4h at the temperature between 25 and 30°C. The resulting precipitate was washed with water and ethanol, respectively. Finally, the product was dried in vacuum at room temperature for 24h.

e) Measurements

The ultrasonic experiments were carried out by an ultrasonic disperser. Scanning Electron Microscopy (FESEM) of PAni/ Fe_3O_4 nanocomposites was performed by JEOL JSM-7600F Field Emission Scanning Electron Microscopy. FTIR characterization was performed using PerkinElmer Spectrum 100 FTIR Spectrometer. Room temperature conductivities of the pressed pellets were measured by the standard Van Der Pauw DC four-probe method which was used to measure the electron transport behavior of PAni nanotubes containing Fe_3O_4 nanoparticles. The samples of PAni/ Fe_3O_4 were pressed into pellet. Then the pellet was cut into a square. The square was placed on the four-probe apparatus. Providing a voltage, a corresponding electrical current was obtained. The electrical conductivity of samples was calculated by the following formula:

$$\sigma \text{ (S/cm)} = (2.44 \times 10/S) \times (I/E) \quad (1)$$

Where σ is the conductivity; S is the sample side area; I is the current passed through outer probes; E is the voltage drop across inner probes (Lu *et al.*, 2006).

3. RESULT AND DISCUSSION

The morphologies of the resulting PAni/ Fe_3O_4 composites containing 5, 10, 15 and 20 wt% Fe_3O_4 are shown in Figure-1. FESEM images reveal that all the samples have the morphologies of nanotubes and the diameters of the samples are similar, and the length of PAni/ Fe_3O_4 nanotubes containing 10 and 15wt% Fe_3O_4 is a little longer than the rest of the samples Figure-1. (b) & (c).

Moreover, the electronic diffraction patterns indicate that the obtained Fe_3O_4 were crystalline. The formation of the nanotube is not regular when 5 and 20 wt% Fe_3O_4 was added to PAni as shown in Figure-1. (a) & (d) respectively, there is also a little aggregation of Fe_3O_4 nanoparticles in the composite nanotubes sample containing 20wt% Fe_3O_4 nanoparticles. Figure-1. (b) However, it still provides a simple method to synthesize PAni/ Fe_3O_4 composite nanotubes containing relatively higher content of Fe_3O_4 nanoparticles.

Table-1 and 2 shows the effects of both Fe_3O_4 and H_3PO_4 respectively on the composites conductivity, when the amount of (H_3PO_4) is increase the pH is reduced, the resulting conductivity at room temperature increases from 7.40×10^{-5} to about 6.06×10^{-3} S/cm as the dopant is increase from 0.05-0.07ml, further increasing of H_3PO_4 results in reduction of the composite's conductivity at room temperature (Table 2). The increase in conductivity may be attributed to increase in the dopant concentration which is believe to be the major factor possibly playing a more important role (Haldorai *et al.*, 2011). The conductivity values obtained are similar to those informed by (Deng, *et al.*, 2003) for PAni- Fe_3O_4 composites with core-shell structure from a magnetic fluid and dodecylbencensulfonic acid sodium salt as a surfactant and dopant for a sample containing 43.86 % magnetic oxide.



The procedure involved in this synthesis of PAni/Fe₃O₄ nanocomposite consists of two steps: the first step is the surface-modification of Fe₃O₄ nanoparticles in order that they will disperse well, and the second step is the ultrasonically assisted chemical oxidative

polymerization of the monomer in the presence of nanoparticles. As mentioned earlier the nanocomposites with different loadings of Fe₃O₄ (5, 10, 15 and 20% w/w) were also carried out.

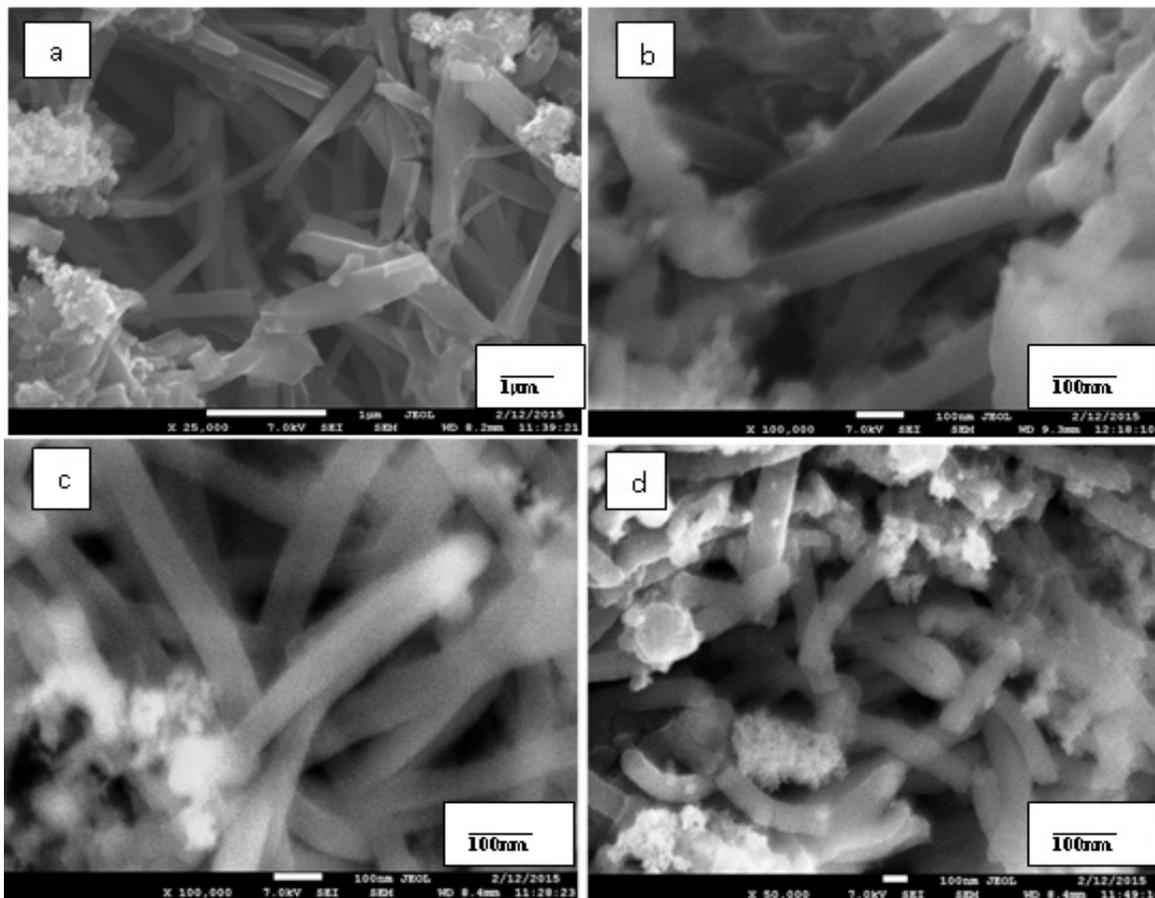


Figure-1. FESEM images of PAni nanotube containing (a) 5wt% (b) 10wt% (c) 15wt% and (d) 20wt% Fe₃O₄ nanoparticles.

After polymerization the solution of aniline, APS, phosphate acid and some quantity of Fe₃O₄ nanoparticles under magnetic stirring, it could only yield PAni/Fe₃O₄ powder, no PAni/Fe₃O₄ nanotubes could be obtained. However, under the ultrasonic irradiation, PAni/Fe₃O₄ composite nanotubes could be observed (Figure-1). This was thought to be attributed to the ultrasonic irradiation.

Lu *et al.* studied the mechanism of PAni nanofibers produced by interfacial polymerization and they thought that PAni preferentially forms as nanofibers in aqueous solution during chemical oxidative polymerization (Lu, *et al.*, 2006). The nanotubes produced in the early stage of polymerization during slow-feeding reactions were subject to secondary growth, which led to the large agglomerates containing irregularly shaped particles. Pure nanotubes could be obtained by preventing the secondary growth. In our method to synthesize PAni,

the secondary growth was prevented effectively after using the ultrasonic irradiation, and nanotube is obtained.

FTIR spectra are used to characterize the molecular structures of PAni/Fe₃O₄ composite nanotubes. Figure-2 shows the characteristic peaks of PAni nanotubes with four different quantity of Fe₃O₄ nanoparticles. The spectrum of pristine Fe₃O₄ had a band at 689 cm⁻¹ ascribed to the Fe–O stretching vibration. It is found that PAni/Fe₃O₄ composite nanotubes have characteristic peaks at around 3124cm⁻¹ (N–H stretching), 1541 cm⁻¹, 1385 cm⁻¹ (C = C stretching deformation of quinoid and benzenoid ring, respectively), 1303 cm⁻¹ (C–N stretching of secondary aromatic amine), 1140cm⁻¹, and 889cm⁻¹ (out-of-plane deformation of C–H in the 1,4-disubstituted benzene ring) which indicate the availability of PAni containing Fe₃O₄. (Figure-2.) All of these peaks are similar to those of PAni synthesized by a common method (Haldorai, *et al.*, 2011). However, the incorporation of



Fe₃O₄ nanoparticles leads to the shift of some FT-IR bands of the PANi. This may be ascribed to the fact that the interaction of Fe₃O₄ and PANi was followed by the

formation of H-bonding between the proton on N-H and the oxygen atom on the Fe₃O₄ surface (Qiu, *et al.*, 2006).

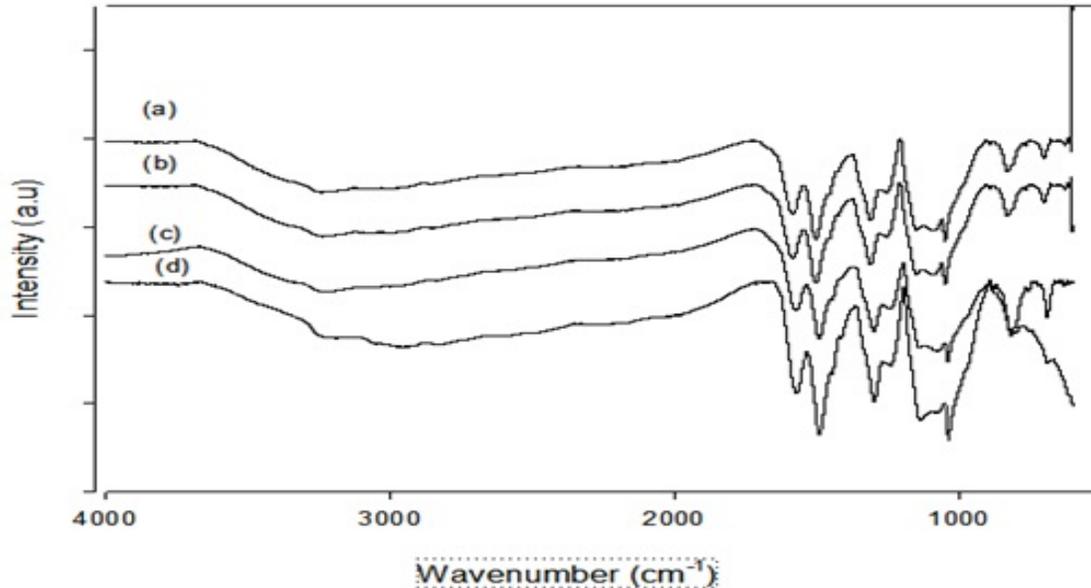


Figure-2. FTIR spectra of PANi nanotubes containing (a) 5 wt% (b) 10wt% (c) 15wt% and (d) 20wt% Fe₃O₄ nanoparticles.

Table-1. Conductivity of PANi with different wt% Fe₃O₄.

Samples	Fe ₃ O ₄ content (wt%)	Conductivity (S/cm)
Pani	---	1.04×10^{-3}
Pristine Fe ₃ O ₄	--	
Pani/Fe ₃ O ₄	(5%)	6.49×10^{-4}
Pani/Fe ₃ O ₄	(10%)	7.46×10^{-4}
Pani/Fe ₃ O ₄	(15%)	6.06×10^{-3}
Pani/Fe ₃ O ₄	(20%)	1.07×10^{-4}

Electrical conductivity measurements of the PANi nanotube and Pani/Fe₃O₄ nanocomposites were carried out using a standard four-point probe apparatus. Fe₃O₄ contents affect the conductivity of the resulting PANi composites. The conductivity of the polyaniline nanotube (PANi) was found to be 1.04×10^{-3} S/cm, while that of nanocomposite with 5, 10, 15 and 20% Fe₃O₄ was found to be 6.49×10^{-4} , 7.46×10^{-4} , 6.06×10^{-3} and 1.07×10^{-4} S/cm, respectively (Table 1). This observation agrees with some earlier reports (Zhang *et al.*, 2005). The decrease in the conductivity of nanocomposites with increasing Fe₃O₄ concentration can be attributed to the insulating behavior of Fe₃O₄ in the core of nanoparticle, which hinders the charge transfer thereby lowering the conductivity.

Table-2. Conductivity of PANi with different amount of H₃PO₄.

Samples	H ₃ PO ₄ (ml)	Conductivity (S/cm)
Pani	--	1.04×10^{-3}
Pristine Fe ₃ O ₄	--	
Pani/Fe ₃ O ₄	0.05	7.46×10^{-5}
Pani/Fe ₃ O ₄	0.06	6.49×10^{-4}
Pani/Fe ₃ O ₄	0.07	3.02×10^{-3}
Pani/Fe ₃ O ₄	0.08	2.07×10^{-4}

Table-1 also shows that when 5% Fe₃O₄ was incorporated into PANi, the conductivity of PANi composite was greatly reduced from 1.04×10^{-3} of pure PANi to 6.49×10^{-4} S/cm. Further increasing of Fe₃O₄ content from 5 to 10 wt.%, results in slight reduction of the conductivity at room temperature. Although at 15wt%, the conductivity is higher than the other values but still slightly lower than the pure PANi. Both the insulating behaviour of iron oxide in the core of the nanoparticle and the decrease in the doping degree is thought to play a major role in the decrease of the room temperature conductivity of the PANi/Fe₃O₄ nanocomposites.



4. CONCLUSIONS

In this study, a simple method to synthesize surface-modified PANi/Fe₃O₄ nanocomposites *via* ultrasonically-assisted chemical oxidative polymerization was demonstrated. Under ultrasonic irradiation, the aggregates of Fe₃O₄ nanoparticles were broken down and the particles were redispersed in aqueous solution, the nanocomposites are found to be stable and electrically conductive. It is therefore possible to prepare a nanocomposite with moderate conductivity that can be used as a conductive matrix for developments of sensors.

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