An Industry Friendly Approach for the Preparation of Magnetic and Electro-Conductive Polyaniline Composite Particles

M. K. Debnath*, H. Ahmad

Department of Chemistry, Rajshahi University, Rajshahi 6205, Bangladesh

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Abstract

Recently nano-sized conducting polymers have gained ample attention because of their unique properties and promising potentiality in nanomaterials and nanodevices. Among the conducting polymers, polyaniline (PANi) is the most studied conducting polymers because of its low monomer cost, ease of preparation, high conductivity in doped form, excellent environmental stability, controllable physical and electrochemical properties by oxidation and protonation. In this investigation magnetic PANi composite particles were prepared following a novel approach by using citric acid for the first time as dopant, surfactant and solubilizing agent. As synthesized citric acid doped Fe$_3$O$_4$ (magnetite)/PANi nanocomposites have been characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffractometer (XRD), Scanning electron microscope (SEM), Thermogravimetry analysis (TGA). Spectroscopic analyses confirmed the modification of Fe$_3$O$_4$ nanoparticles by PANi layer. The Magnetic susceptibility results revealed the paramagnetic behavior of Fe$_3$O$_4$/PANi nanocomposite particles. The electrical conductivities of Fe$_3$O$_4$/PANi nanocomposites increased up to certain amount of Fe$_3$O$_4$ and decreased thereafter.

Keywords: Conducting polymer; Citric acid; Oxidative polymerization; Magnetic and Electro-conductive nanocomposite.

1. Introduction

Polymeric nanocomposites possessing both conducting and ferromagnetic functions are especially useful because they frequently exhibit unexpected hybrid properties synergistically derived from both components [1-3]. The control and design of characteristic structural features on the nanometer scale impart them with tailored properties for diverse applications [4]. Hence interest in the design and controlled fabrication of these composite materials with superior conducting and ferromagnetic properties are continuously increasing [5]. Over the past decades, polyaniline (PANi) has

*Corresponding author: mk15debnath@yahoo.com
emerged as one of the most promising organic conducting polymers, owing to its high conductivity and exhibits dramatic changes in its electronic structure and physical property in its protonated state [5]. In addition to these unique properties of PANi, it is highly stable in air. Therefore, several approaches to synthesize nanocomposite consisting of magnetic nanoparticles and conducting PANi have been reported [6-8]. But most of the researchers have synthesized magnetic PANi using either strong inorganic acids viz. phosphoric acid/HCl/H₂SO₄/dodecyl benzene sulfonic acid sodium salt, DBSA etc. Here DBSA also functioned as a stabilizer in addition to dopant as well [9-11]. All of the strong inorganic acids are environmentally harmful and corrosive to health, skin and expensive. The focal objective of this investigation is to find a less expensive, industry friendly, environmentally benign and economically feasible method for the preparation of electromagnetic PANi nanocomposite particles without using strong inorganic acid. Therefore in this study efforts have been given to synthesize magnetic PANi following a new approach by using citric acid for the first time as surfactant, dopant and solvent. Citric acid is a mild organic acid, less harmful to environment and inexpensive compared to the chemicals reported in the literature. In this study a simple two-step process was applied for the preparation of citric acid doped Fe₃O₄/PANi nanocomposite particles. In the first step nano-sized Fe₃O₄ particles were prepared by co-precipitation of Fe²⁺ and Fe³⁺ from their alkaline solutions. Then in the second step Fe₃O₄/PANi nanocomposite particles were prepared by seeded chemical oxidative polymerization of aniline in presence of variable amount of Fe₃O₄ contents using ammonium persulfate (APS) as an oxidant and citric acid as dopant, surfactant and solvent. The schematic illustration for the preparation of Fe₃O₄/PANi nanocomposite particles is shown in Scheme 1.

Scheme 1. Reaction scheme for the preparation of Fe₃O₄/PANi nanocomposite particles.
2. Experimental

2.1. Monomers and chemicals

Aniline of monomer grade, purchased from Thomas Baker, (Chemicals) Limited, India, was used without any purification. Ferric chloride (FeCl₃), ferrous sulphate heptahydrate (FeSO₄·7H₂O), citric acid, ammonium persulphate (APS) and ammonium hydroxide (NH₄OH) and other chemicals were of analar grade. Deionized water was distilled using a glass distillation apparatus.

2.2. Instruments

Scanning Electron Microscope, SEM (Hitachi, SU8000, Japan) was used to see the morphology and particle size distribution. IR spectrophotometer, FTIR (Perkin Elmer, FTIR-100, UK), Thermal analyses were carried out using thermal analyzer, TGA (STA 8000, Perkin Elmer, Netherland), XRD (Raigaku, RINT D/max-kA), were used for the analysis of composite structure Sherwood Scientific Magnetic Susceptibility Balance were used for magnetic property analysis. The conductivity of Fe₃O₄/PANi nanocomposites were measured using the Agilent, PIA-4294A, USA, impedance analyzer at room temperature with operating frequency 100 Hz to 10 MHz.

2.3. Methodology

2.3.1. Synthesis of Fe₃O₄ nano-seed particles by co-precipitation method

Nano-sized Fe₃O₄ seed particles were prepared by co-precipitation of Fe²⁺ and Fe³⁺ from their aqueous solutions (molar ratio 1:1.87) using 25% NH₄OH. For this purpose, FeSO₄·7H₂O (2.855 g) and FeCl₃ (3.127 g) were dissolved in water (90 g). Solutions were then transferred to a 250 mL three necked round flask followed by addition of 25% NH₄OH (54.05 g) maintained at 25°C under a nitrogen atmosphere for 2 h. The reaction mixture was stirred at around 800 rpm with a magnetic stirrer. The prepared Fe₃O₄ suspension was treated with (2 M) HNO₃ (10.0 g) for 15 min and washed with water until the supernatant was neutral. The black colored particles exhibited a strong magnetic response. The produced Fe₃O₄ nanoparticles were dried at 70°C.

2.3.2. Preparation of Fe₃O₄/PANi nanocomposite particles

Variable amounts (0.2, 0.3 and 0.6 g) of Fe₃O₄ nanoparticles as seed were taken in 100 g citric acid (2 M) solution and sonicated for 30 min to make dispersion. Fe₃O₄ dispersion was then transferred to a 250 mL conical flask maintained at 25°C under a nitrogen atmosphere. Aniline (1.0 g) was added and the mixture was magnetically stirred at ~200 rpm for 10 min to completely dissolve the monomer prior to the addition of APS as oxidant. After the addition of APS, the stirring was continued for 6 hr to complete the
reaction. The composite particles were washed with 0.2 M HCl for removing any non-encapsulated Fe\textsubscript{3}O\textsubscript{4} particles. The product was purified by repeated centrifugation and decantation, replacing the continuous phase by de-ionized distilled water.

3. Results and Discussion

3.1. Structural characterization

The chemical structure of obtained product was determined by FT-IR spectrum. Fig. 1 represents the IR spectra of PANi particles and Fe\textsubscript{3}O\textsubscript{4}/PANi nanocomposite particles prepared with variable Fe\textsubscript{3}O\textsubscript{4} contents. Since Fe\textsubscript{3}O\textsubscript{4} belongs to inverse spinel structure, Fe\textsuperscript{3+} ions are situated in two different lattice sites. The absorption bands at 583 and 435 cm\textsuperscript{-1} could therefore be attributed to the intrinsic Fe–O vibrations of tetrahedral and octahedral Fe\textsuperscript{3+}, respectively [12,13]. The peaks at 3,465 and 3,139 cm\textsuperscript{-1} are ascribed to N–H stretching vibrations of amino groups in the structural units of the PANi, while the peaks at 1,560 and 1,500 cm\textsuperscript{-1} are due to the C=C stretching vibration of quinoid rings and benzenoid ring units respectively [13]. The presence of these peaks confirms that the prepared PANi is composed of both amine and the imine units. In the IR spectrum of PANi, the absorption band at 1293 cm\textsuperscript{-1} shows the C-N stretching of secondary aromatic amine [14]. The signal at 1131 cm\textsuperscript{-1} corresponds to B-NH-B, where B refers to the benzenic type ring [15]. In the IR spectra of Fe\textsubscript{3}O\textsubscript{4}/PANi nanocomposite particles the characteristic peaks of PANi and Fe\textsubscript{3}O\textsubscript{4} are present but show slight shifting toward lower wave number. This may be ascribed to the fact that the interaction of Fe\textsubscript{3}O\textsubscript{4} and PANi was followed by the formation of H-bonding between the proton on N–H and the oxygen atom on the Fe\textsubscript{3}O\textsubscript{4} surface [16].

![FT-IR spectra](image)

Fig. 1. FT-IR spectra of a) PANi particles and Fe\textsubscript{3}O\textsubscript{4}/PANi nanocomposite particles prepared with variable Fe\textsubscript{3}O\textsubscript{4} contents (g); b) 0.2; c) 0.3; d) 0.6.
3.2. Surface morphology

Fig. 2 represents the SEM images Fe$_3$O$_4$/PANi nanocomposite particles prepared in presence of variable amount of Fe$_3$O$_4$ nano-seed particles with the aniline content in the recipe remained fixed. It is evident that Fe$_3$O$_4$ content critically determined the morphology as well as stability of the composite particles. Relative to PANi content the presence of increasing amount of Fe$_3$O$_4$ nano-seed particles reduces the tendency of aggregation. Irrespective of iron oxide content the composite particles remained mostly spherical or semi-spherical. In the case of highest Fe$_3$O$_4$ (0.6 g) content Fe$_3$O$_4$/PANi composite particles were found to align in a chain like fibre structure. The average particle sizes measured from SEM photographs are ~50 nm for Fe$_3$O$_4$ nano-seed particles and ~161, ~179, and ~165 nm for those of Fe$_3$O$_4$/PANi nanocomposite particles prepared with 0.2, 0.3 and 0.6 g of Fe$_3$O$_4$ nano-seed particles respectively. The increase in diameter implies that chemical oxidative polymerization occurred mostly at the surface of Fe$_3$O$_4$ nanoparticles.

![SEM images](image)

Fig. 2. SEM images of a) Fe$_3$O$_4$ nano-seed particles and Fe$_3$O$_4$/PANi nanocomposites prepared in presence of variable amount of Fe$_3$O$_4$ (g); b) 0.2; c) 0.3 and d) 0.6.

3.3. X-ray diffraction

X-ray diffraction (XRD) studies on the composites reveal the inclusion of Fe$_3$O$_4$ particles in the composites [17]. Fig. 3 represents the XRD patterns of Fe$_3$O$_4$/PANi nanocomposite particles prepared with variable Fe$_3$O$_4$ contents. The profile exhibited peaks assignable to reflections due to Fe$_3$O$_4$ at two theta values of 36.39°, 44.36°, 57.32° and 63.75° are observed only for composite particles prepared by using higher Fe$_3$O$_4$ contents (0.3 and 0.6 g). The absence of diffraction signals at lower Fe$_3$O$_4$ contents is attributed to complete surface coverage with dense PANi shell layer. The characteristic peaks of Fe$_3$O$_4$ nanoparticles are little broad and less intense, indicating the concealment of the crystalline behavior of Fe$_3$O$_4$ attributed to its encapsulation by PANi [18]. Moreover, the XRD
pattern is dominated by a broad signal at two theta value of 21.3° and 26.78°, which are similar with those usually observe for amorphous PANi [19,20].

Fig. 3. XRD diffraction patterns of Fe₃O₄/PANi nanocomposite particles prepared with variable Fe₃O₄ contents (g): a) 0.2; b) 0.3; c) 0.6.

3.4. Thermo-gravimetric analysis

Fig. 4 shows the TGA curves for Fe₃O₄ nano-seed particles and Fe₃O₄/PANi nanocomposite particles prepared with variable iron oxide contents. The mass loss of the reference Fe₃O₄ nano-seed particles reached about 7.6% at 800°C. This mass loss is associated with the removal of adsorbed water [21]. In the case of Fe₃O₄/PANi nano composite particles the organic PANi is expected to burn off completely at 800°C and the residual part would represent inorganic Fe₃O₄ content. It is observed from the Fig. 4. that overall weight loss of composite particles decreased with the increase of Fe₃O₄ content and hence more Fe₃O₄ is incorporated. The residual mass at 800°C for composite particles prepared with 0.2 g Fe₃O₄ is negligibly small (~1.4%). But at relatively higher Fe₃O₄ content, the residual mass increased to ~7.5 and ~17% respectively. This themogravimetric analysis suggests that fairly large amount of Fe₃O₄ can be encapsulated in Fe₃O₄/PANi nanocomposite particles by controlling the magnetite/aniline ratio during seeded chemical oxidative polymerization.

3.5. Magnetic property of the samples

Magnetic susceptibility gives idea about magnetic nature. Table 1 shows the values of magnetic susceptibility for Fe₃O₄/PANi nanocomposite particles. The value of magnetic susceptibility increases with the increase of magnetite content. The positive value indicates that irrespective of Fe₃O₄ content the composite particles are strongly paramagnetic.
Fig. 4. TGA curves for Fe$_3$O$_4$ nanoparticles and Fe$_3$O$_4$/PANi nanocomposite composite particles prepared with variable Fe$_3$O$_4$ contents (g).

Table 1. Magnetic susceptibility of various particles.

<table>
<thead>
<tr>
<th>Nanocomposite particles</th>
<th>Fe$_3$O$_4$ (g)</th>
<th>PANi (g)</th>
<th>Magnetic susceptibility ($\chi_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$/PANi</td>
<td>0.2</td>
<td>1.0</td>
<td>4.02×10$^{-5}$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/PANi</td>
<td>0.3</td>
<td>1.0</td>
<td>4.79×10$^{-5}$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/PANi</td>
<td>0.6</td>
<td>1.0</td>
<td>1.17×10$^{-4}$</td>
</tr>
</tbody>
</table>

3.6. Electrical conductivity

Table 2 shows the effect of Fe$_3$O$_4$ on the conductivity of Fe$_3$O$_4$/PANi nanocomposite particles. It can be observed that the values of conductivities increase up to 0.3 g of Fe$_3$O$_4$ in PANi and decreases thereafter. The initial increase up to 0.3 g Fe$_3$O$_4$ is attributed to the extended chain length of PANi, where polaron possesses sufficient energy to hop between favourable localized sites. As the amount of Fe$_3$O$_4$ increases beyond 0.3, the partial blocking of charge carrier hop occurs and as a result conductivity decreases [22].

Table 2. Electrical conductivity of various particles.

<table>
<thead>
<tr>
<th>Nanocomposite particles</th>
<th>Amount of Fe$_3$O$_4$ (g)</th>
<th>Amount of PANi (g)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$/PANi</td>
<td>0.2</td>
<td>1.0</td>
<td>1.06×10$^{-3}$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/PANi</td>
<td>0.3</td>
<td>1.0</td>
<td>5.3×10$^{-3}$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/PANi</td>
<td>0.6</td>
<td>1.0</td>
<td>3.2×10$^{-3}$</td>
</tr>
</tbody>
</table>
4. Conclusion

In this research, it was attempted to prepare and characterize magnetic and electro-conductive Fe$_3$O$_4$/PANi nanocomposite particles. The Fe$_3$O$_4$/PANi magnetic and electro-conductive nanocomposite nanoparticles with a diameter of ~161-179 nm were prepared via an in situ polymerization of aniline in an aqueous solution containing the Fe$_3$O$_4$ magnetic fluid. The synthesized Fe$_3$O$_4$/PANi nanocomposite particles were confirmed from their detailed characterization by FT-IR spectra, TGA thermograms, SEM images, XRD diffraction patterns, magnetic susceptibility results and conductivity data. From the magnetic susceptibility and conductivity data it was found that Fe$_3$O$_4$/PANi nanocomposite particles are magnetic and electro-conductive in nature.

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