JSR Publications

Available Online

J. Sci. Res. **9** (4), 403-411 (2017)

JOURNAL OF SCIENTIFIC RESEARCH

www.banglajol.info/index.php/JSR

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

Received 31 May 2017, accepted in final revised form 16 September 2017

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_3O_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_3O_4 nanoparticles by PANi layer. The Magnetic susceptibility results revealed the paramagnetic behavior of Fe_3O_4/PANi nanocomposite particles. The electrical conductivities of Fe_3O_4/PANi nanocomposites increased up to certain amount of Fe_3O_4 and decreased thereafter.

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

doi:4http://dx.doi.org/10.3329/jsr.v9i4.32724 J. Sci. Res. **9** (4), 403-411 (2017)

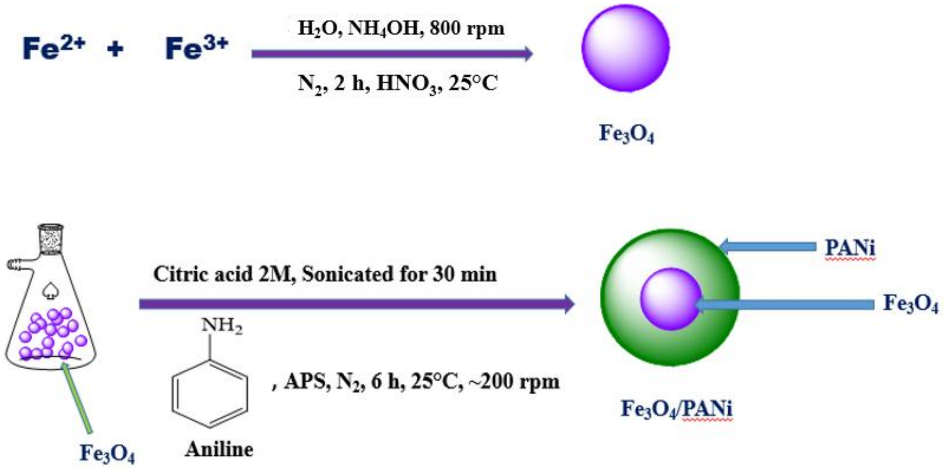
1. Introduction

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/H_2SO_4/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 electro-magnetic 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 Fe_3O_4/PANi nanocomposite particles. In the first step nano-sized Fe_3O_4 particles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} from their alkaline solutions. Then in the second step Fe_3O_4/PANi nanocomposite particles were prepared by seeded chemical oxidative polymerization of aniline in presence of variable amount of Fe_3O_4 contents using ammonium persulfate (APS) as an oxidant and citric acid as dopant, surfactant and solvent. The schematic illustration for the preparation of Fe_3O_4/PANi nanocomposite particles is shown in Scheme 1.



Scheme 1. Reaction scheme for the preparation of Fe_3O_4/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 ($FeCl_3$), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), citric acid, ammonium persulphate (APS) and ammonium hydroxide (NH_4OH) 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 Fe_3O_4/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 Fe_3O_4 nano-seed particles by co-precipitation method*

Nano-sized Fe_3O_4 seed particles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} from their aqueous solutions (molar ratio 1:1.87) using 25% NH_4OH. For this purpose, $FeSO_4.7H_2O$ (2.855 g) and $FeCl_3$ (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% NH_4OH (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 Fe_3O_4 suspension was treated with (2 M) HNO_3 (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 Fe_3O_4 nanoparticles were dried at 70°C.

2.3.2. *Preparation of Fe_3O_4/PANi nanocomposite particles*

Variable amounts (0.2, 0.3 and 0.6 g) of Fe_3O_4 nanoparticles as seed were taken in 100 g citric acid (2 M) solution and sonicated for 30 min to make dispersion. Fe_3O_4 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_3O_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_3O_4/PANi nanocomposite particles prepared with variable Fe_3O_4 contents. Since Fe_3O_4 belongs to inverse spinel structure, Fe^{3+} ions are situated in two different lattice sites. The absorption bands at 583 and 435 cm^{-1} could therefore be attributed to the intrinsic Fe–O vibrations of tetrahedral and octahedral Fe^{3+}, respectively [12,13]. The peaks at 3,465 and 3,139 cm^{-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^{-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^{-1} shows the C-N stretching of secondary aromatic amine [14]. The signal at 1131 cm^{-1} corresponds to B-NH-B, where B refers to the benzenic type ring [15]. In the IR spectra of Fe_3O_4/PANi nanocomposite particles the characteristic peaks of PANi and Fe_3O_4 are present but show slight shifting toward lower wave number. This may be ascribed to the fact that the interaction of Fe_3O_4 and PANi was followed by the formation of H-bonding between the proton on N–H and the oxygen atom on the Fe_3O_4 surface [16].

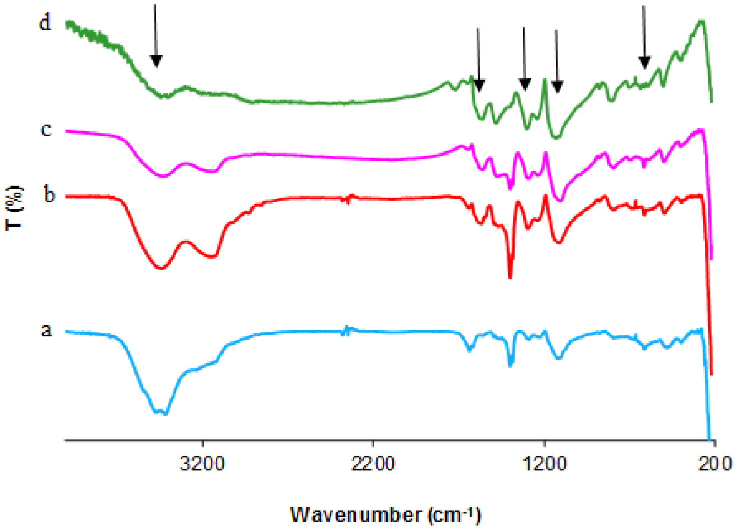


Fig. 1. FT-IR spectra of a) PANi particles and Fe_3O_4/PANi nanocomposite particles prepared with variable Fe_3O_4 contents (g); b) 0.2; c) 0.3; d) 0.6.

3.2. *Surface morphology*

Fig. 2 represents the SEM images Fe_3O_4/PANi nanocomposite particles prepared in presence of variable amount of Fe_3O_4 nano-seed particles with the aniline content in the recipe remained fixed. It is evident that Fe_3O_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_3O_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_3O_4 (0.6 g) content Fe_3O_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_3O_4 nano-seed particles and ~161, ~179, and ~165 nm for those of Fe_3O_4/PANi nanocomposite particles prepared with 0.2, 0.3 and 0.6 g of Fe_3O_4 nano-seed particles respectively. The increase in diameter implies that chemical oxidative polymerization occurred mostly at the surface of Fe_3O_4 nanoparticles.

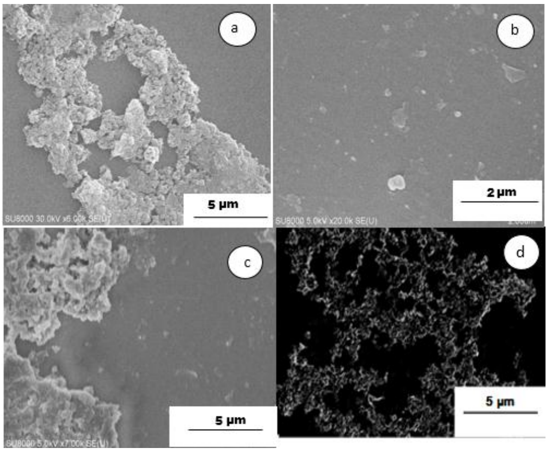


Fig. 2. SEM images of a) Fe_3O_4 nano-seed particles and Fe_3O_4/PANi nanocomposites prepared in presence of variable amount of Fe_3O_4 (g); b) 0.2; c) 0.3 and d) 0.6.

3.3. *X-ray diffraction*

X-ray diffraction (XRD) studies on the composites reveal the inclusion of Fe_3O_4 particles in the composites [17]. Fig. 3 represents the XRD patterns of Fe_3O_4/PANi nanocomposite particles prepared with variable Fe_3O_4 contents. The profile exhibited peaks assignable to reflections due to Fe_3O_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_3O_4 contents (0.3 and 0.6 g). The absence of diffraction signals at lower Fe_3O_4 contents is attributed to complete surface coverage with dense PANi shell layer. The characteristic peaks of Fe_3O_4 nanoparticles are little broad and less intense, indicating the concealment of the crystalline behavior of Fe_3O_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].

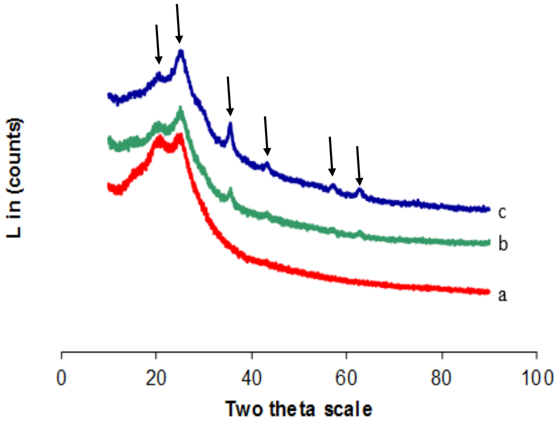


Fig. 3**.** XRD diffraction patterns of Fe_3O_4/PANi nanocomposite particles prepared with variable Fe_3O_4 contents (g): a) 0.2; b) 0.3; c) 0.6.

3.4. *Thermo-gravimetric analysis*

Fig. 4 shows the TGA curves for Fe_3O_4 nano-seed particles and Fe_3O_4/PANi nanocomposite particles prepared with variable iron oxide contents. The mass loss of the reference Fe_3O_4 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 Fe_3O_4/PANi nano composite particles the organic PANi is expected to burn off completely at 800°C and the residual part would represent inorganic Fe_3O_4 content. It is observed from the Fig. 4. that overall weight loss of composite particles decreased with the increase of Fe_3O_4 content and hence more Fe_3O_4 is incorporated. The residual mass at 800°C for composite particles prepared with 0.2 g Fe_3O_4 is negligibly small (~1.4%). But at relatively higher Fe_3O_4 content, the residual mass increased to ~7.5 and ~17% respectively. This themogravimetric analysis suggests that fairly large amount of Fe_3O_4 can be encapsulated in Fe_3O_4/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 Fe_3O_4/PANi nanocomposite particles. The value of magnetic susceptibility increases with the increase of magnetite content. The positive value indicates that irrespective of Fe_3O_4 content the composite particles are strongly paramagnetic.

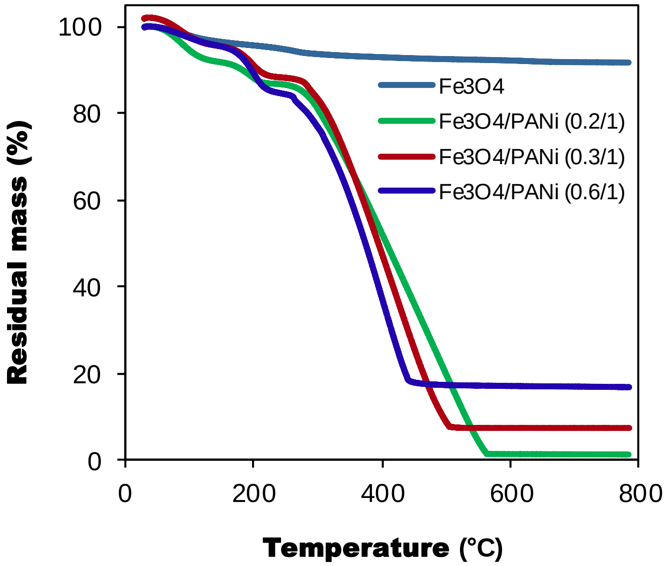


Fig. 4. TGA curves for Fe_3O_4 nanoparticles and Fe_3O_4/PANi nanocomposite composite particles prepared with variable Fe_3O_4 contents (g).

Table 1. Magnetic susceptibility of various particles.

Nanocomposite particles	Fe_3O_4 (g)	PANi (g)	Magnetic susceptibility (χ_g)
Fe_3O_4/PANi	0.2	1.0	4.02×10^{-5}
Fe_3O_4/PANi	0.3	1.0	4.79×10^{-5}
Fe_3O_4/PANi	0.6	1.0	1.17×10^{-4}

3.6. *Electrical conductivity*

Table 2 shows the effect of Fe_3O_4 on the conductivity of Fe_3O_4/PANi nanocomposite particles. It can be observed that the values of conductivities increase up to 0.3 g of Fe_3O_4 in PANi and decreases thereafter. The initial increase up to 0.3 g Fe_3O_4 is attributed to the extended chain length of PANi, where polarons possess sufficient energy to hop between favourable localized sites. As the amount of Fe_3O_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.

Nanocomposite particles	Amount of Fe_3O_4 (g)	Amount of PANi (g)	Conductivity (S/cm)
Fe_3O_4/PANi	0.2	1.0	1.06×10^{-3}
Fe_3O_4/PANi	0.3	1.0	5.3×10^{-3}
Fe_3O_4/PANi	0.6	1.0	3.2×10^{-3}

4. Conclusion

In this research, it was attempted to prepare and characterize magnetic and electro-conductive Fe_3O_4/PANi nanocomposite particles. The Fe_3O_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_3O_4 magnetic fluid. The synthesized Fe_3O_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_3O_4/PANi nanocomposite particles are magnetic and electro-conductive in nature.

Acknowledgment

Authors would like to acknowledge Central Science Laboratory, Rajshahi University, Rajshahi; Dr. Klaus Tauer, MPI of Colloid & Interfaces, Germany; Dr. Hideto Minami, Associate Professor, Graduate School of Science and Technology, Kobe University, Japan; Md. Abdur Rahman Ph.D. student, Yamagata University, Japan, for instrumental support.

References

1. N. N. Mallikarjuna, S. K. Manohar, P. V. Kulkarni, A. Venkataraman, and T. M. Aminabhavi, J. Appl. Polym. Sci. **97**, 1868 (2005). https://doi.org/10.1002/app.21405
2. A. Maity and M. Biswas, J. Appl. Polym. Sci. **94**, 803 (2004). https://doi.org/10.1002/app.20944
3. M. Alenxandre and P. Dunois, Mater. Sci. Eng. **28**, 1 (2000). https://doi.org/10.1016/S0927-796X(00)00012-7
4. C. C. Holmes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, Science **293**, 673 (2001). https://doi.org/10.1126/science.1061655
5. J. Deng, Y. Peng, C. He, X. Long, P. Li, and A. S. C. Chan, Polym. Int. **52**, 1182 (2003). https://doi.org/10.1002/pi.1237
6. R. F. Mancilla, J. T. E. Galindo, E. V. Santiago, C. A. H. Escobar, A. V. Rios, and E. A. Z. Contreras, Int. J Theore. Appl. Nanotechnol. **4**, 1 (2016).
7. D. L. Zhao, H. L. Zhang, X. W. Zeng, Q. S. Xia, and J. T. Tang. Biomed. Mater. **1**, 198 (2006). https://doi.org/10.1088/1748-6041/1/4/002
8. H. Gu, Y. Huang, Xi Zhang, Q. Wang, J. Zhu, L. Shao, N. Haldolaarachchige, D. P. Young , S. Wei, and Z. Guo, Polymer **53**, 801 (2012). https://doi.org/10.1016/j.polymer.2011.12.033
9. M. Petrychuk, V. Konvalenko, A. Pud, N. Ogurtsov, and A. Gubin, Phys. status. Solid. **207**, 442 (2010). https://doi.org/10.1002/pssa.200824421
10. F. G. d. Souza Jr, J. A. Marins, J. C. Pinto. G. E. d. Oliveira, C. M. Rodrigues, and L. M. T. R. Lima, J. Mater. Sci. **45**, 5012 (2010).
11. S. H. Hosseini, R. Rahimi, and H. Kerdari, Polym. J. **43**, 745 (2011). https://doi.org/10.1038/pj.2011.47
12. K. Basavaiah, Y. P. Kumar, and A. V. P. Rao, Appl. Nanosci. **12**, 148 (2012).
13. D. R. Devi, Y. P. Kumar, and K. Basavaiah, Int. J. Sci. Res. **5(10),** 2319 (2016).
14. S. Xuan, Y. X. J. Wang, K. C. F. Leung, and K Shu, J. Phys. Chem. **112**, 18804 (2008).
15. Y. Li, C. Zhu and J. Kan, Metals **5**, 2403 (2015). https://doi.org/10.3390/met5020547

16. M. A. Adamu, M. K. Mustafa, and N. N. B. Ruslan, ARPN J. Eng. Appl. Sci. **11**, 16 (2016).
17. S. Radhakrishnan, S. Prakash, Chepuri R. K. Rao, and M. Vijayan. Electrochem. Solid-State Lett. **12**, 84 (2009). https://doi.org/10.1149/1.3074315
18. S. Kumar and S. Jain, J. Chem. Article ID 837682 (2014).
19. L. Zhang, M. Wan, and Y. Wei. Macromol. Rapid Commun. **27**, 366 (2006). https://doi.org/10.1002/marc.200690045
20. Z. Taghipoura, H. Eisazadeh, and M. Tanzifi, Int. J. Eng. **27**, 227 (2014).
21. N. Arsalani, H. Fattahi, and M. Nazarpoor, eXPRESS Polym. Lett. **4**, 329 (2010). https://doi.org/10.3144/expresspolymlett.2010.42
22. S. Khasim, S. C. Raghavendra, M. Revanasiddappa, K. C. Sajjan, M. Lakshmi, and M. Faisal, Bull. Mater. Sci. **34**, 1557 (2011). https://doi.org/10.1007/s12034-011-0358-z