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Synthesis of Polyaniline/γ-Fe_2O_3 Nanocomposites and Study of their Structural and Electrical Properties

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ABSTRACT

Conducting nanocomposites of polyaniline/maghemite (PANI/γ-Fe_2O_3) have successfully prepared with different weight percentages of γ-Fe_2O_3 (0-0.5 wt. %) by adopting chemical oxidation route at 5ºC. These nanocomposites were characterized for their structure, morphology and dc electrical conductivity by fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) and standard two point probe method respectively. It can be clearly seen that dispersion of γ-Fe_2O_3 has imparted good structural and conducting properties in PANI matrix. The percolation threshold for dc electrical conductivity was found at 0.3% filling of maghemite contents in PANI chains.

1. INTRODUCTION

After the discovery of conducting polymers in 1977 (Tan 2009), research on functional pi-conjugated systems has promptly grownup as an extensive multidisciplinary field inclusive of solid state physics, organic chemistry, electrochemistry and photo-physics due to their novel electrical and mechanical properties (Kima 2002). Conjugated polymer nanocomposites take account of a new generation of multifunctional material since one decade to enhance their functionality and processibility; subsidize to form technologically advanced materials with miscellaneous functionalities for device implementation and for their potential applications (Fu 2012), (Fu 2011), (Kumar 2011). These conducting polymers upon doping exhibit very high electrical conductivity comparable to metals and offered variety of applications towards technology that includes rechargeable batteries, conductive adhesive, photovoltaic devices, light emitting diodes (LEDs), sensors (Batool 2012),

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corrosion inhibitors (Chung 2009), electromagnetic interference (EMI) shielding (Binitha 2011), diodes and transistor (Ahujaa 2007).

Polyaniline (PANI) has received great deal of attention because of its unique properties such as lightweight, outstanding environmental and thermal stability, easy polymerization and the low cost of the monomer (Michira 2007). Amongst inorganic nano-fillers, maghemite is one of the most widely used magnetic materials because of its interesting magnetic properties as well as widespread potential applications in soft magnetic materials, magnetic recording media and ferrofluids. These remarkable properties have made it suitable for its potential application to be used in microelectronics (Msieh 2006).

The aim of this work is the preparation of polymer/ferrite nanocomposites with γ-Fe_2O_3 as the chemical composition. The microstructural and conducting properties of the nano-material have been investigated by different characterization techniques in order to understand their behavior.

2. EXPERIMENTAL PROCEDURE

2.1. Chemicals

Aniline (Riedel-deHaën) was purified before polymerization and stored in an inert environment at 4ºC. Other chemicals like ammonium per sulphate (APS) (Analytical grade), ferric chloride ($FeCl_3$) (Analytical grade) and hydrochloric acid (35.5 %) (Analar) was used as received without further purification. All the solutions were prepared in doubly distilled water.

2.2. Synthesis of Maghemite Nanoparticles

The maghemite nanopartices used were synthesized by adding ammonia into an aqueous solution of $FeCl_3$ and $FeCl_2$ (Ferroudj 2013). Then, the successive addition of HNO_3 and $Fe(NO_3)_3$ has oxidized synthesized magnetite into maghemite nanoparticles.

2.3. Synthesis of PANI

0.15M of aniline was added drop wise into 150 ml of 0.6 M solution of APS and allowed to stir for 24 hours at 5ºC to complete polymerization of aniline monomer. The resulting dark green precipitates of conducting polyaniline were vacuum filtered and washed with 2M HCl, aceton and deionized water to remove any oligomer of unreacted aniline. Finally the synthesized PANI was dried at room temperature for 12 hours.

2.4. Synthesis of PANI/γ-Fe_2O_3 Composites

As synthesized maghemite nanoparticles (0.1 g) were dispersed in 0.6 M solution of APS and stirred for 15 minutes. Then 0.15M aniline was syringed in the above reaction mixture at room temperature under continuous stirring of 24 hours to get PANI/γ-Fe_2O_3 composite and abbreviated as PNC-0.1%. Other composites of PANI with various weight percentages of γ-Fe_2O_3 (0.2-0.5 wt.%) were prepared by dispersing 0.2 g, 0.3 g, 0.4 g and 0.5 g nanoparticles in the oxidant solution and named as PNC- 0.2%, PNC-0.3%, PNC-0.4% and PNC-0.5% respectively.

3. INSTRUMENTS AND CHARACTERIZATIONS

The FT-IR spectra of all prepared nanocomposites were recorded by Perkin Elmer RXI FT-IR spectrophotometer in the normal IR region 4000-650 cm^{-1} and 4 cm^{-1} band resolutions at room temperature.

Room temperature electrical measurements were carried out by semiconductor characterization system CSC 4200 S by using formula:

$$\sigma\left(S.cm^{-1}\right)=\frac{\pi}{\ln 2}\frac{\left(F\times I\right)}{\left(V\times T\right)} \quad (1)$$

Here F is the shape factor, T is the thickness of film, V is the applied voltage and I is the corresponding flow of current across it.

Scanning electron microscopy (SEM) images were obtained by Hitachi S-3400 for microstructural analysis operated at secondary electron image mode at an accelerating voltage of 25kV.

3.1. FT-IR analysis

Fig. 1 shows the FT-IR spectra of PANI and PANI/γ-Fe_2O_3 composites. FTIR spectrum of PANI shows the main characteristic peaks at 3426, 1514, 1456, 1294, 1132, 1031 and 675 cm^{-1}. The peak at 3426 cm^{-1} could be attributed to N-H stretching mode (Vivekanandan 2011). The bands at 1514 and 1456 cm^{-1} are attributed to stretching vibrations of N=Q=N ring (Deng 2013) and N-B-N ring (Xia 2002) respectively. The bands at 1294 and 1132 cm^{-1} correspond to N-H bending and the symmetric component of the C-C stretching modes (Gupta 2005). The peak at 1031 cm^{-1} assigned to C-N stretching of secondary aromatic amine (Qi 2011). The characteristic peak at 675 cm^{-1} in the spectra of γ-Fe_2O_3 ascribed to the bending vibrations of the γ-Fe_2O_3 crystal lattice and was observed in all PANI/Fe_2O_3 composites. Fig. 1(b-e) shows the shifting of all characteristic bands of PANI towards higher frequencies to confirm an increase in conjugation chain length and some physiochemical interactions between PANI and dispersing phase in PANI/γ-Fe_2O_3 composites (Bandgar 2007).

A comparison was performed between polyaniline and its nanocomposites to illustrate the effect of nanoparticles loading on the electrical conductivity of PANI matrix by using standard two point probe technique. Room temperature dc conductivities of PANI and its composites with varied weight percentages of maghemite (0-0.5%) were calculated to be 11.02, 23.80, 31.54, 43.51, 16.81, and 10.94 $mS.cm^{-1}$ respectively. All prepared composites showed higher values of conductivity than bare PANI with dramatic increase in electrical conductivity for PNC-0.3% nanocomposite (Fig. 2). This mean that 0.3 % filler concentration facilitates the transport of charge carrier through the polymer chain by bringing better compactness/packing of the polymer chains by

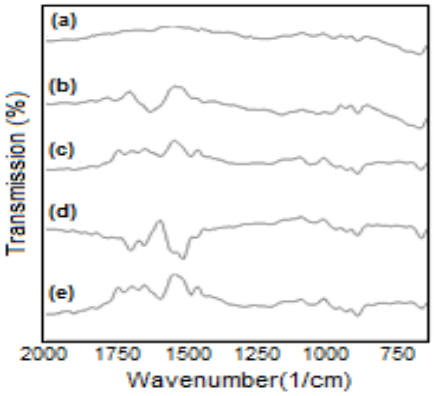

Fig. 1 FT-IR spectra of (a) γ-Fe_2O_3 (b) PNC-0.1% (c) PNC-0.2% (d) PNC-0.3% (e) PNC- 0.5%

3.2. Conductivity measurements

nanoparticles to enhanced its conductivity. Conductivity decreased for proceeding composites with high loading of γ-Fe_2O_3 nanoparticles. It may be due to increase of insulating phase that opposed low energy transitions of donor electrons.

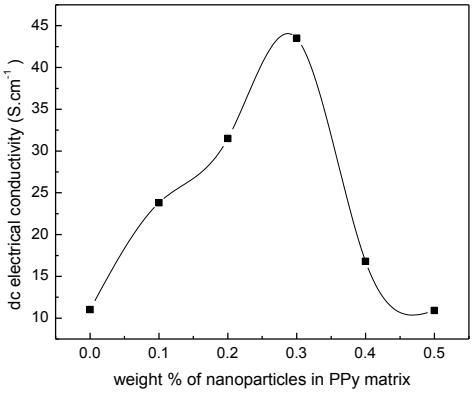

Fig. 2 DC electrical conductivity as a function of Nanoparticle loading percentage

3.3. SEM Analysis

Fig. 3a shows the SEM micrograph of bare polyaniline with globular morphology and spherical particles of size ~ 1μm slanted over each other. Formation of composite with 0.3 wt.% loading of maghemite contents brought compactness and decreased the density of porosity in the polymer structure and has increased the grain size from 1.6μm as shown in Figure 3c. This micrograph also reveals the homogeneous dispersion of crystallite domains supported on long polymeric chains consequently carry charge transportation. Figure 3d clearly depicts that high dispersive concentration of aluminium oxide particles in PNS-0.5% that caused poor connectivity between the grains and inhomogeneous dispersion as well that affected to fall its dc conductivity.

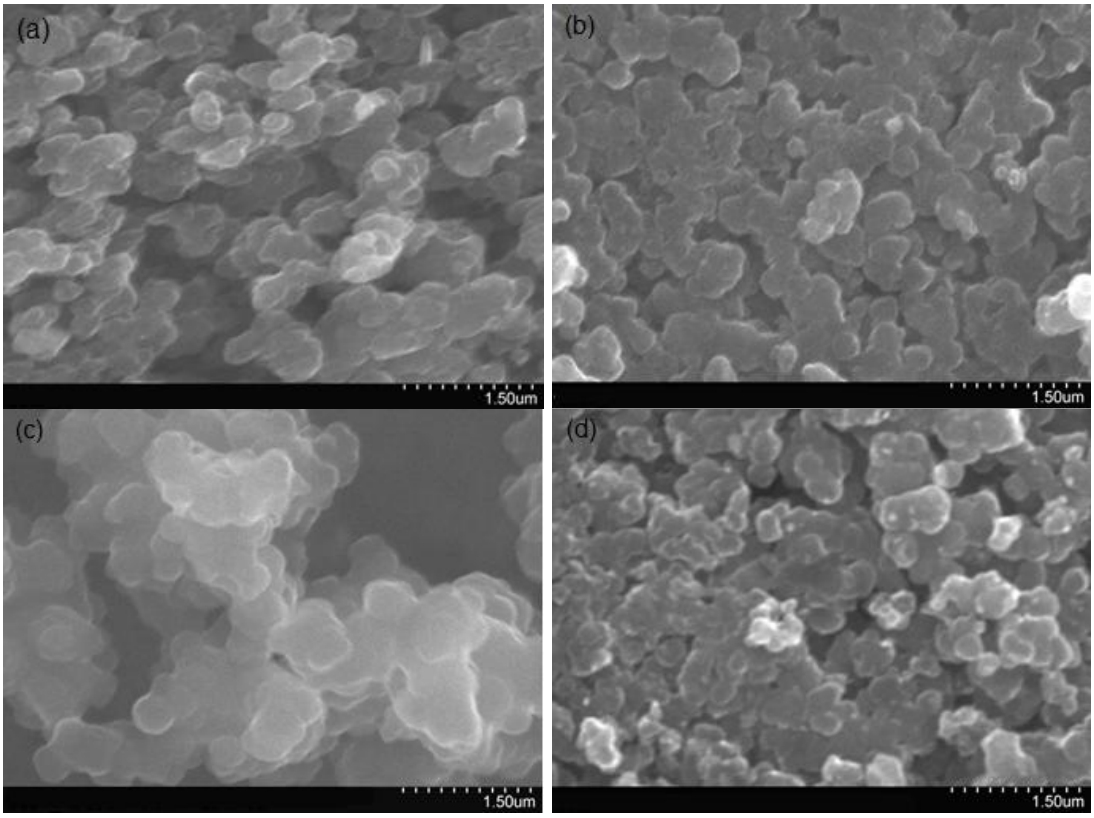

Fig. 3 SEM micrographs of (a) PANI (b) PNC-0.1% (c) PNC-0.3% (d) PNC-0.5%

4. **CONCLUSIONS**

Investigations on heterogeneous polymer system that the different weight percentages of nanopartices affected the molecular structure of polymer matrix to change its physical and physiochemical properties. Incorporation of γ-Fe_2O_3 has increased its grain size with the filler loading percentage. Filler dispersion up to 0.3 wt.% level offered maximum conductivity by producing better interactions between the filler particles and the polymer back bone and assisted the transport of charge carrier through the polymer chain due to homogeneous dispersion of γ-phase in polymer chain to provide packing network as inferred from FT-IR and SEM analysis.

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