Characterization of Polyaniline/Fe_3O_4-Polyacrylonitrile Composite Nanofibers

Hui Qiao, Fang Chen, Xin Xia, Qu-Fu Wei*, Feng-Lin Huang

Key Laboratory of Eco-Textiles, Ministry of Education, Jiangnan University, Wuxi 214122, P.R. China

Abstract: Polyaniline/Fe_3O_4 nanoparticle composite was prepared by microemulsion in-situ polymerizing aniline in the presence of Fe_3O_4 nanoparticles upon the use of ammonium persulfate(APS) as the initiator, hydrochloric acid(HCl) as intermingling acid, cetyltrimethylammonium bromide (CTAB) as emulsifying agent and normal butanol as auxiliary emulsifying agent. The results revealed that a core-shell structure composite was obtained successfully. Further more, pure PANI solution was not able to be electrospun into the fibrous structure, so electrospinning of emeraldine base Fe_3O_4-polyaniline/ polyacrylonitrile (Fe_3O_4-PANI/PAN) blends with different composition ratios were performed using N,N-Dimethylformamide as solvent. Morphology and fibers diameters were investigated by scanning electronic microscopy (SEM). The fibers with diameter ranging from 168 to 300 nm were obtained. The ratio of polyaniline/ Fe_3O_4 to PAN was fixed at 3:8. Scanning electron microscopy indicated that the diameter of the composite nanofiber increased with the content of Fe_3O_4.

Keywords: Microemulsion, polyaniline, Fe_3O_4, electrospinning, nanocomposite fiber.

1. Introduction

Conductive polymers compounded with nano-inorganic composite have attracted a great deal of attention in recent years. The obtained composite materials have superior properties, such as magnetism and conductivity. Nanoinorganic particles were usually coated by polymers to prevent agglomerating due to their high surface activity [1-2]. The nanoinorganic Fe_3O_4 particles adopted in this article is a kind of anti-spinal ferrite, which can be widely used as soft magnetic materials. PANI is one of the commonly used conductive polymers due to its excellent conducting performance, good environ-mental stability, cheaper and unique doping mechanism. It can also be easily synthesized with high production rate and diverse molecular structures. Organic-inorganic hybrid materials exhibiting both electric and magnetic properties, which can be widely, used as electromagnetic shielding and microwave absorption materials.

Electrospnning has become a simple and inexpensive technique to produce sub-micron fibers and nanofibers, the nanofibers fabricated in this way has evenly distributed diameters. However it remains a great challenge to apply electrospinning to PANI limited by its molecular weight and solubility. PANI blended with other polymers have been tried to form nanofibers using electrospinning technique [3-5]. Doping Fe_3O_4 in PANI makes the composite nanofiber possess integrated properties of both conductivity and magnetism. In this paper, PANI and inorganic particles were homogeneously mixed by adding Fe_3O_4 nanoparticles into the aniline solution during its microemulsion polymerization. With the help of the cation surface active agent CTAB, Fe_3O_4 could be better coated by PANI. Fe_3O_4/PANI composite with regular structures, good stability, favourable solubility in organic solution, and high electric conductivity was obtained by this way. The spinning solution was prepared by mixing Fe_3O_4/PANI with PAN [6-9]. The existence of PAN greatly improved the spinnability of the PANI solution. The Fe_3O_4/PANI composite materials have great potential in applications like electrode materials, sensor, microwave absorption, etc.

2. Experiment

2.1 Materials

Aniline monomer was distilled twice under reduced pressure before use. The other reagents such as $(NH_4)_2S_2O_8$ (APS, as initiator of polymerization), CTAB, n-Butyl Alcohol, polyethylene glycol (PEG, M_W=4000) and polyacrylonitrile (PAN, M_W=20000 ~30000) were used without any purification.

2.2 Preparation of Fe_3O_4 nanoparticles

25 ml 0.4 M $FeCl_3$ $6H_2O$ aqueous solution and 50 ml 0.3 M $FeSO_4$ $\cdot 7H_2O$ aqueous solution were mixed to form a new uniform solution. 13g PEG was then added into the solution and sonicated for several minutes to

*Corresponding author's email: qfwei@jiangnan.edu.cn
JFBI Vol. 2 No. 4 2010 doi:10.3993/jfbi03201008

let it dissolve homogenously. Under stirring at 70 ℃, ammonia water was added in drops to get the pH value up to 9. Then the reaction solution was stirred at 70 ℃ for 2hrs, and then separated with magnet to obtain Fe_3O_4 nanoparticles. The obtained Fe_3O_4 nanoparticles were rinsed with distilled water for several times and dried in vacuum at 40 ℃ for 24 hrs.

2.3 Synthesis of PANI/Fe_3O_4 nanocomposites

PANI/Fe_3O_4 nanocomposites were synthesized via *in-situ* polymerization at 0~5℃ as follows. In a typical procedure, 0.562g Fe_3O_4 nanoparticles, 7.782g CTAB and 9.56ml n-Butyl Alcohol were added into 50 ml water and sonicated at room temperature for about 3hrs for the Fe_3O_4 nanoparticles to disperse homogeneously. 2.2ml aniline monomer was then dissolved in the above suspension and stirred for 1h. The oxidant ammonium peroxydisulfate previously dissolved in 30mL HCl solution(1 mol/L), was cooled and dropped into the reaction medium for over 30 min. The reaction was carried out at 0-5 ℃ for another 20 hrs. Then the reaction mixture was filtered and rinsed with distilled water for several times and methanol for once. Finally, the obtained black powder was dried in vacuum at 40 ℃ for 24 hrs.

2.4 Preparation of PANI/Fe_3O_4–PAN nano-fibers

The PANI/Fe_3O_4-PAN spinning solution was prepared by dissolving PAN chips in DMF and then blending it with PANI/Fe_3O_4 nanoparticles. The electrospinning apparatus is shown in Figure 1.

Figure 1 System setup for electrospinning process.

The hypodermic syringe used in these experiments had a capillary tip diameter of 20 gauges. A positive potential was applied to the PANI/Fe_3O_4 -PAN solution by connecting a copper wire to the metal capillary and the potential difference between the syringe and the counter electrode (collector) was 15 kV. A rotating drum covered with aluminium foil, placed 15 cm below the capillary tip, was used to collect the electrospun material.

2.5 Characterization

High-resolution transmission electron microscopy (HRTEM) images were obtained by JEM-2010 and JEM-2100 transmission electron microscopes. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Fourier transform infrared spectrometer. X-ray diffraction (XRD) analysis was conducted on a powder Philips PW1830 diffractometer with CuKα radiation. The thermal property was analyzed with a thermogravimetric analyzer of TA 51 TGA of TA Instrument. TGA analysis was performed at 100~750℃with 20 ℃/min in air.

3. Results and discussion

Figure 2 shows the HRTEM images of pure Fe_3O_4 nanoparticles and PANI/Fe_3O_4 nanocomposites. As shown in Figure 2(a), pure Fe_3O_4 nanoparticles look spherical with an average diameter of about 10nm. Figure 2(b) indicates that all Fe_3O_4 nanoparticles are covered by PANI, and the Fe_3O_4 nanopaticles encapsulated by PANI are also spherical with an average size of about 10nm, which is similar to the pure Fe_3O_4 nanopaticles shown in Figure 2(a). This phenomenon is attributed to several reasons. The interaction between Fe_3O_4 nanopaticles and PANI has a positive effect on the encapsulation of Fe_3O_4 by PANI. On the other hand, the addition of cationic surfactant CTAB also plays a very important role for the coating of Fe_3O_4 nanopaticles by PANI.

That is because cationic surfactant CTAB is absorbed and arranged regularly on the surface of Fe_3O_4 to inhibit Fe_3O_4 nanopaticles from depositing and gathering together [10-11]. On the other hand, $(NH_4)_2S_2O_8$ (APS) was used as initiator during the polymerization. When APS is added, the negative electric charge $S_2O_8^{2-}$ from APS could combine with the positive electric charge CTA^+ from CTAB, thus some heavy floccules of insoluble substance appears instantly due to the production of the insoluble $(CTA)_2S_2O_8$. Therefore the floccules of insoluble substance will cover the surface of Fe_3O_4 nanopaticles. Moreover, oxidative polymerization will occur on the surface of $(CTA)_2S_2O_8$ when aniline monomer arrives on the surface of (CTA) $_2S_2O_8$ through Brownian