Polyaniline/Fe$_3$O$_4$ Magnetic Nanocomposite Prepared by Ultrasonic Irradiation

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ABSTRACT: Ultrasonic irradiation is employed to assist the chemical oxidative polymerization of aniline in the presence of Fe$_3$O$_4$ nanoparticles in order to prepare a polyaniline (PANI)/Fe$_3$O$_4$ magnetic nanocomposite. In the chemical oxidative polymerization of aniline in the initially neutral medium, the optimum molar ratio of the oxidant ammonium persulfate to the monomer aniline is 2 : 1. The prepared PANI is in the emeraldine form and is doped by sulfate anions. Fe$_3$O$_4$ particles are encapsulated by PANI and dispersed well in PANI. Fe$_3$O$_4$ increases the doping level and decreases the crystallinity of PANI. The PANI/Fe$_3$O$_4$ nanocomposite possesses conductivity and magnetic properties. Increasing the Fe$_3$O$_4$ content increases the magnetization of the PANI/Fe$_3$O$_4$ composite but decreases its conductivity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2107–2111, 2006

Key words: chemical oxidative polymerization; magnetic; polyaniline; ultrasonic irradiation

INTRODUCTION

Conducting polymer composites with electrical and magnetic properties have potential applications in batteries, electrochemical display devices, electromagnetic interference shielding, electromagnetorheological fluids, and microwave-absorbing materials. Polyaniline (PANI) is an important conducting polymer with unique electrical, optical, and optoelectrical properties, as well as excellent environmental stability.[1] Iron oxide is a well-known magnetic material. Thus, a PANI/iron oxide composite hopefully possesses both electrical and magnetic properties. Several approaches have been developed to prepare such a composite: blending PANI and iron oxide in a solid state or liquid medium[2]; coprecipitating a suspension containing Fe^{2+}, Fe^{3+}, and PANI by adjusting the pH values to precipitate Fe^{2+} and Fe^{3+} into maghemite and magnetite[3–5]; and *in situ* polymerizing a monomer in the presence of iron oxide particles.[6–11] For *in situ* polymerization, the challenges are how to avoid the aggregation of iron oxide nanoparticles and the large loss of iron oxide. Therefore, a surfactant or stabilizer is usually used and strong acid should be avoided. Deng et al.[8] prepared magnetic and conducting Fe$_3$O$_4$–PANI nanoparticles using sodium dodecylbenzene sulfonate (SDBS) as a surfactant and dopant. They also prepared Fe$_3$O$_4$-

crosslinked PANI nanoparticles using poly(ethylene glycol) as a surfactant.[9] Cheng et al.[11] synthesized a Fe$_3$O$_4$–PANI nanocomposite in SDBS–HCl aqueous solution using SDBS as a surfactant and dispersant.

In the present study, the ultrasonic irradiation technique was employed to prepare a PANI/Fe$_3$O$_4$ nanocomposite with electrical and magnetic properties by *in situ* polymerization of aniline in the presence of Fe$_3$O$_4$ nanoparticles.

Ultrasound has been widely used in chemical reactions, such as dispersion, emulsifying, crushing, organic synthesis, and polymerization; this is because ultrasonic cavitation can generate local temperatures as high as 5000 K and local pressures as high as 500 atm, with heating and cooling rates greater than 10^9 K/s, which is a very rigorous environment.[12] Ultrasonic irradiation is a useful technique for preparing novel materials with unusual properties. The application of ultrasound to prepare conducting PANI and conducting polymer composites has been reported.[13–17] Compared to PANI prepared by conventional stirring, PANI prepared by ultrasonic irradiation has higher conductivity[13,14] or higher crystallinity.[15] In our previous studies,[16,17] we also prepared PANI/TiO$_2$ and PANI/SiO$_2$ composites with a core–shell structure under ultrasonic irradiation.

In this study the polymerization of aniline was begun by the addition of an oxidant, ammonium persulfate (APS), in the initially neutral medium whereas Fe$_3$O$_4$ nanoparticles were dispersed on the nanoscale by ultrasonic irradiation. Synthesized PANI deposited on the surfaces of the Fe$_3$O$_4$ particles, and PANI/Fe$_3$O$_4$ composite particles with the structure of PANI encapsulating

TABLE I
Yield and Conductivity of PANI at Different Mole Ratios of APS to Aniline in Initially Neutral Medium

	Molar ratio of APS/aniline				
	1	1.5	2	2.5	3
Yield (%)	29.4	53.9	83.7	96.0	90.9
Conductivity $(S\ cm^{-1})$	4.9×10^{-3}	4.8×10^{-2}	0.21	0.15	0.13

Fe_3O_4 were formed. The influences of Fe_3O_4 nanoparticles on the structural, electrical, and magnetic properties of the PANI/Fe_3O_4 composite were investigated.

EXPERIMENTAL

Materials and apparatus

The Fe_3O_4 nanoparticles were prepared by the chemical coprecipitation method of $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ in poly(vinylpyrrolidone) aqueous solution under ultrasonic irradiation.[18] Aniline (Chengdu Chemical Reagent Factory) was analytical grade, distilled under reduced pressure, and stored at 0°C for use. APS [$(NH_4)_2S_2O_8$, Chengdu Chemical Reagent Factory] was analytical grade and used as received.

A model VCF-1500 ultrasonic generator (Sonics & Materials) was employed. The schematic diagram of the ultrasonic reactor was described in a previous article.[19]

Preparation of PANI by ultrasonic irradiation

The chemical oxidative polymerization of aniline was carried out at an initial pH 7. Desired amounts of aniline and water were added into the ultrasonic reactor. The cooling water was circulated, and the ultrasonic generator was switched on. A desired volume of $(NH_4)_2S_2O_8$ oxidant solution was added dropwise.

After 30 min the ultrasound was stopped. During the reaction process, the N_2 flow rate was maintained at 30 mL min^{-1}, cooling water was circulated to maintain 10°C, and the ultrasound power output was 750 W. The final product was filtrated, washed with deionized water, and then vacuum dried at 80°C for 12 h.

Preparation of PANI/Fe_3O_4 composite by ultrasonic irradiation

Desired amounts of Fe_3O_4 nanoparticles, aniline, and water were introduced into the ultrasonic reactor. The ultrasound was switched on, and the APS oxidant was added dropwise. The molar ratio of APS to aniline was 2 : 1 in all experiments. After 30 min the ultrasonic generator was switched off. The reaction conditions were the same as the preparation of PANI through ultrasonic irradiation. The final products were filtrated, washed with deionized water, and vacuum dried at 80°C for 12 h.

Characterization

The conductivities of pressed pellets of the PANI/Fe_3O_4 composite and PANI were measured using an SDY-4 four-point probe apparatus (Guangzhou Semiconductor Materials Institute, Guangzhou, China) at ambient temperature. Transmission electron microscopy (TEM) analysis was conducted on a JEM 100-CX instrument.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos XSAM-800 electron spectrometer with a Al X-ray source. In spectral deconvolution, linear backgrounds were subtracted and synthetic Gaussian–Lorentzian (80–20%) components were fitted to the data. The widths (full width at half-maximum) of the individual lines were kept constant. Atomic concentrations were determined using peak area ratios corrected by experimentally determined sensitivity factors.
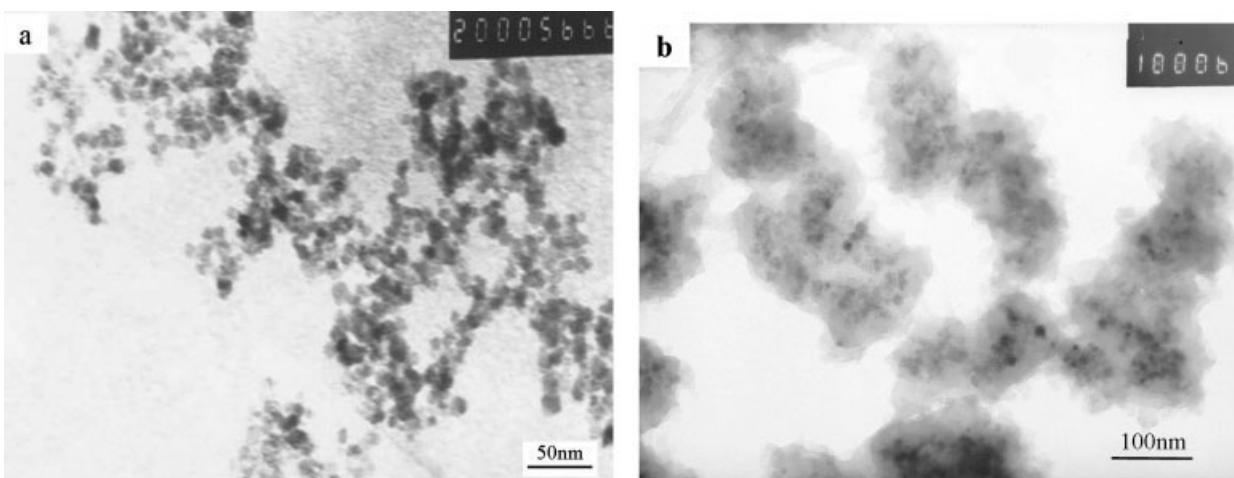

Figure 1   TEM photos of (a) Fe_3O_4 nanoparticles and (b) the PANI/Fe_3O_4 composite with 37.8% Fe_3O_4.

X-ray diffraction (XRD) analysis was conducted on an X'pert Pro MPD diffractometer using Cu Kα radiation. Magnetization curves were measured using a JDM-13 vibrating sample magnetometer in magnetic fields up to 15 kOe at room temperature.

RESULTS AND DISCUSSION

Preparation of PANI by ultrasonic irradiation in initially neutral medium

In a typical synthesis of PANI by chemical oxidative polymerization, the reaction of aniline proceeds in a strongly acidic medium wherein APS is usually an oxidant and acid is a dopant.[1,2,20] However, acid erodes Fe$_3$O$_4$. In order to decrease the loss of Fe$_3$O$_4$ during the preparation process of the PANI/Fe$_3$O$_4$ composite, the polymerization of aniline must be carried out in an initially neutral medium. Gospodinova et al.[21] studied the oxidative polymerization of aniline in an initially neutral medium. The polymerization of aniline resulted in a sharp decrease in the pH of the medium. The conductivity of PANI was about 10^{-3} S cm^{-1} when the molar ratio of oxidant to aniline was 1 and the monomer concentration was 0.2 mol L^{-1}.

In the chemical oxidative polymerization of aniline in the initially neutral medium under ultrasonic irradiation, the effects of the molar ratio of APS to aniline on the yield and conductivity of PANI are provided in Table I. With the increase in the amount of APS oxidant, the yield and conductivity of PANI first increased and then decreased. The maximal yield and conductivity of PANI was exhibited with 2.5 : 1 and 2 : 1 molar ratios of oxidant to aniline, respectively. In the polymerization of aniline in the initially neutral medium, APS acts as an oxidant as well as the source of dopant.[22] The APS oxidant is reduced to produce sulfate anions, which serve as a dopant[23–25] and increase the conductivity of PANI. With a small amount of APS added, APS is quickly consumed and the polymeriza-
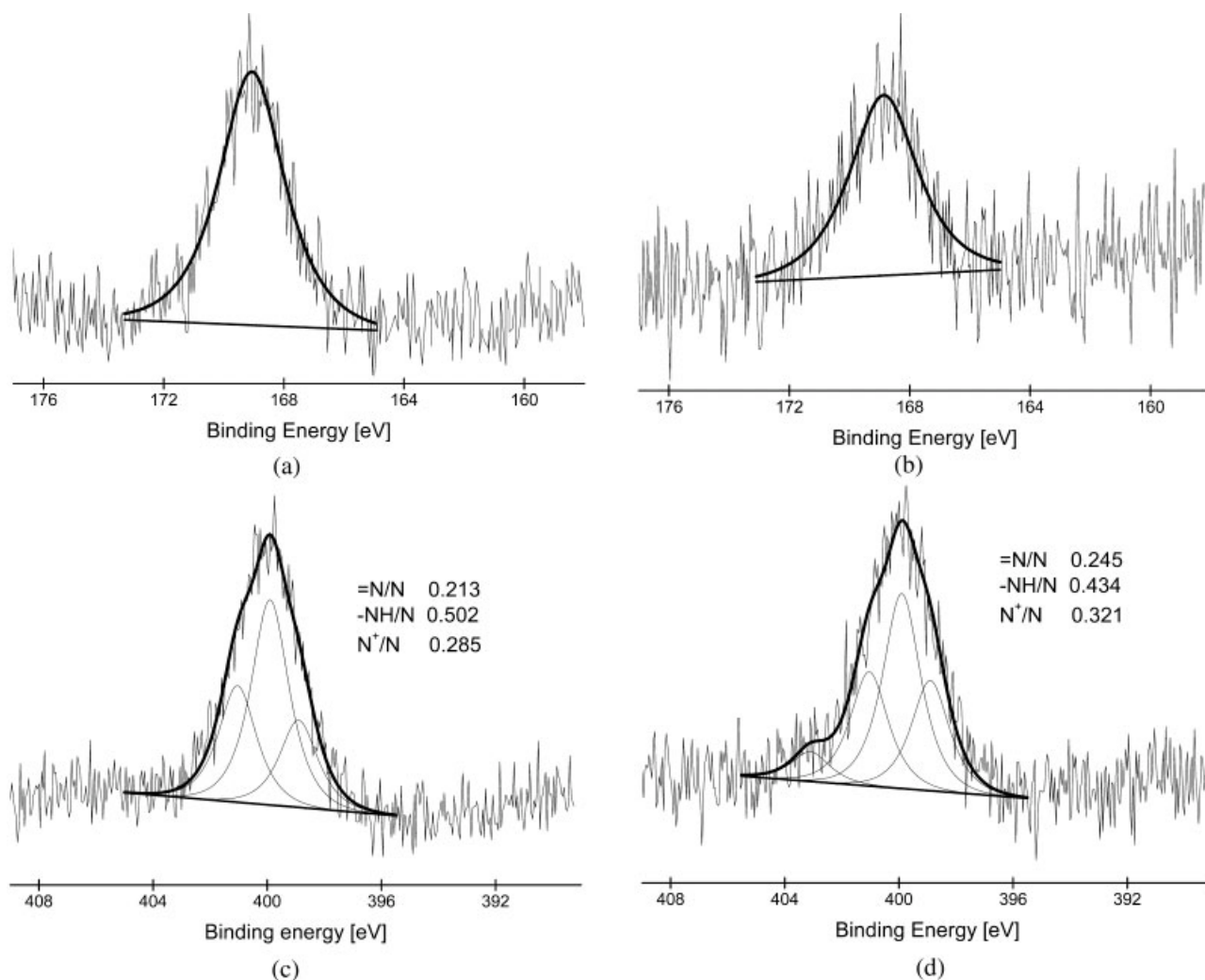

Figure 2 The S2s core-level spectra of (a) PANI and (b) the PANI/Fe$_3$O$_4$ composite and the N1s core-level spectra of (c) PANI and (d) the PANI/Fe$_3$O$_4$ composite with 37.8% Fe$_3$O$_4$.

tion of aniline is not complete, resulting in a low yield of PANI. In addition, sulfate anions from the decomposition of APS are low, resulting in a low doping level and conductivity of PANI. Increasing the amount of APS increases the amount of formed sulfate anions, as well as the doping level and conductivity of PANI. However, an excessively high molar ratio of APS to aniline will result in the overoxidation of PANI, with a concomitant decrease in yield and conductivity.[20]

Morphology and structure of PANI/Fe₃O₄ composite prepared by ultrasonic irradiation

TEM photos of Fe_3O_4 nanoparticles and the PANI/Fe_3O_4 composite are shown in Figure 1. The diameter of the Fe_3O_4 nanoparticles is about 10 nm. The TEM photo of the PANI/Fe_3O_4 composite shows that all Fe_3O_4 nanoparticles are encapsulated by PANI, and there are no separated Fe_3O_4 nanoparticles. The Fe_3O_4 nanoparticles disperse well in PANI because ultrasonic irradiation can break down the aggregation of Fe_3O_4 nanoparticles and make them disperse on the nanoscale during the polymerization of aniline. The formation of PANI-encapsulating Fe_3O_4 composite particles is attributable to the strong interaction between PANI and Fe_3O_4. Under the intense dispersion and stirring effects of ultrasonic irradiation, Fe_3O_4 nanoparticles are dispersed on the nanoscale in the reaction system. After the addition of APS oxidant, the polymerization of monomer aniline begins. The hydrogen bonding and coordinate interaction between Fe_3O_4 and PANI chains favor the absorption of PANI on the surface of Fe_3O_4, which leads to the formation of PANI-encapsulating Fe_3O_4 composite particles. PANI absorbing on the surface of Fe_3O_4 prevents H^+, which was produced by the decomposition of APS, from corroding Fe_3O_4 and decreases the loss of Fe_3O_4.

Figure 2 shows the S2s core-level spectra and N1s core-level spectra of PANI and the PANI/Fe_3O_4 nanocomposite. The peak with the binding energy of 168.9 eV in the XPS spectra of PANI and the PANI/Fe_3O_4 composite is assigned to the sulfur element of sulfate anions, showing that PANI is doped by sulfate anions. Generally, the N atoms of PANI chains are divided into three different nitrogen species: imine nitrogen (=N—), amine nitrogen (—NH—), and positively charged nitrogen (N^+). In the N1s core-level spectra of PANI and the PANI/Fe_3O_4 composite, the major peak at the binding energy of 399.9 eV is attributed to the amine nitrogen (—NH—) of the benzenzoid ring. The peak at 398.9 eV is assigned to the imine nitrogen (=N—) of the quinoid ring. The two peaks above 400 eV are assigned to the positively charged nitrogen (N^+) structure.[26] The existence of a quinoid ring (Q) and a benzenoid ring (B) indicates that PANI prepared in the initially neutral medium is in the emeraldine

form.[1,27] XPS results also indicate the number of quinoid imine units is more than the number of benzenoid imine units. The ratio of —NH/N of PANI is 50% and =N—/N is only 21% because the quinoide imine (—N=) is preferentially protonated when PANI is doped.[24] The doping level of PANI is calculated from the ratio of the peak area of N^+ to the total N1s.[26] The doping level of PANI in the PANI/Fe_3O_4 composite is 0.321, which is higher than that in neat PANI (0.285). Compared to neat PANI, the doping level (N^+/N) of the PANI/Fe_3O_4 composite increases, —NH/N decreases, and =N/N is almost constant. This is due to the interaction of Fe_3O_4 with the —NH of PANI chains. Iron is a transition metal and it has an intense tendency to form coordination bonds with the —NH of PANI chains. Moreover, it is easy to form hydrogen bonding between the O of Fe_3O_4 and the —NH of PANI.

Figure 3 shows XRD curves of PANI, the PANI/Fe_3O_4 composite, and Fe_3O_4 nanoparticles. The peaks of Fe_3O_4 nanoparticles are at 30.1, 35.6, 43.2, 53.8, 57.2, and 62.9°. The crystallite size of the particles can be estimated by XRD using the Scherrer formula.[6] When the peak at 2θ 35.6° is chosen to calculate the crystallite size, the crystallite size of Fe_3O_4 particles is about 8.7 nm. The peaks at 2θ 21 and 24.7° in the XRD curve of PANI show that PANI is partially crystalline. In the XRD curve of the PANI/Fe_3O_4 composite, the main peaks at 2θ 30.2, 35.6, 43.3, 53.6, 57.3, and 62.9° are similar to the main peaks of Fe_3O_4 particles. The broad diffraction peak of PANI is very weak, showing that the crystallinity of PANI in the PANI/Fe_3O_4 composite is much lower than that of neat PANI. Thus, the presence of Fe_3O_4 in the polymerization system strongly affects the crystalline behavior of the formed PANI; that is, the interactions of PANI and Fe_3O_4 nanoparticles restrict the crystallization of PANI.
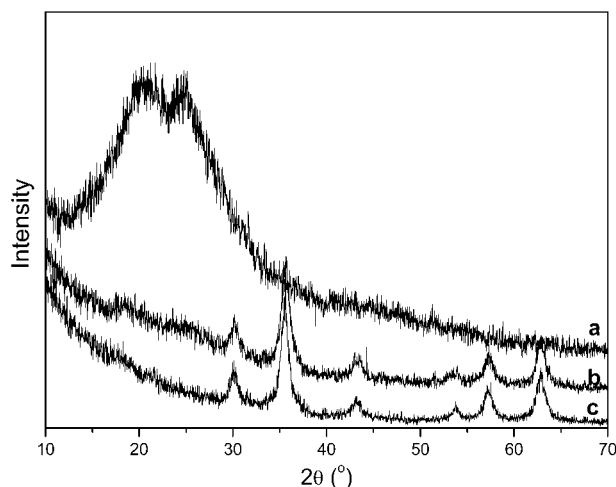

Figure 3　XRD curves of (a) PANI prepared by ultrasonic irradiation, (b) the PANI/Fe_3O_4 composite with 37.8% Fe_3O_4, and (c) Fe_3O_4 nanoparticles.
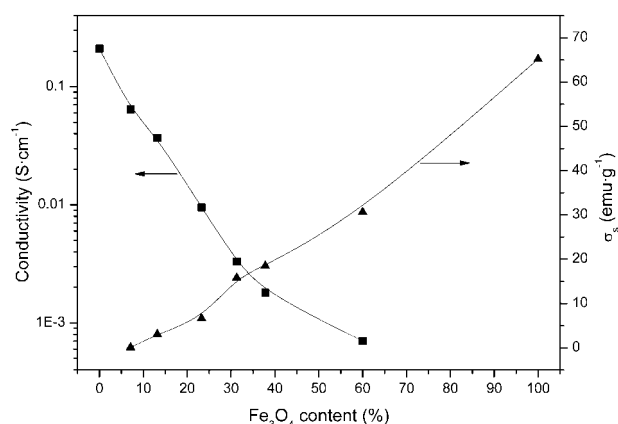
Figure 4 The variation of the conductivity and magnetic properties of PANI/Fe$_3$O$_4$ composites with the Fe$_3$O$_4$ content.

Electrical and magnetic properties of PANI/Fe$_3$O$_4$ composite

Figure 4 shows the effect of the Fe$_3$O$_4$ content on the conductivity and magnetic properties of the PANI/Fe$_3$O$_4$ composite. The conductivity and magnetic properties of the PANI/Fe$_3$O$_4$ composite can be adjusted by changing the Fe$_3$O$_4$ content. Increasing the Fe$_3$O$_4$ content decreases the conductivity and increases the magnetic properties of the PANI/Fe$_3$O$_4$ composite. With the increase in the Fe$_3$O$_4$ content from 7.1 to 60.0%, the conductivity decreases from 6.4×10^{-2} to 7.04×10^{-4} S cm^{-1}, and the saturation magnetization (σ_s) increases from 0.06 to 30.6 emu g^{-1}. The decrease of the conductivity is mainly due to the addition of nonconducting Fe$_3$O$_4$ nanoparticles that decrease the conducting PANI content of the PANI/Fe$_3$O$_4$ composite and partially baffle the formation of conductive paths.

CONCLUSION

A PANI/Fe$_3$O$_4$ nanocomposite with electrical and magnetic properties was successfully prepared by chemical oxidative polymerization in the presence of Fe$_3$O$_4$ nanoparticles under ultrasonic irradiation. PANI prepared with a 2 : 1 APS/aniline molar ratio in the initially neutral medium was in the emeraldine form and was doped by sulfate anions. In the PANI/Fe$_3$O$_4$ nanocomposite all Fe$_3$O$_4$ nanoparticles were encapsulated by PANI. The introduction of Fe$_3$O$_4$ nanoparticles increased the doping level of PANI, hampered the crys-

talline behavior of PANI, and decreased the crystallinity of PANI. Increasing the Fe$_3$O$_4$ content decreased the conductivity and increased the magnetization of the PANI/Fe$_3$O$_4$ composite.

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