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Magnetic and conducting Fe_3O_4–cross-linked polyaniline nanoparticles with core–shell structure

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Abstract

Magnetic and conducting Fe_3O_4–cross-linked polyaniline (CLPANI) nanoparticles with core–shell structure have been prepared in the presence of magnetic fluid in aqueous containing polyethylene glycol as a surfactant. The magnetic properties of the resulting composites showed ferromagnetic behavior, such as high-saturated magnetization ($M_s = 4.22$–19.22 emu/g), and coercive force ($H_c = 2$–8 Oe). The saturated magnetization increased with the increasing of Fe_3O_4 content. The conductivity of the composites at room temperature depended on the Fe content and doping degree. A structural characterization by elemental analysis, Fourier transform infrared, transmission electron micrograph (TEM) and X-ray diffraction proved that nanometer-sized (about 10 nm) Fe_3O_4 in the composites was responsible for the ferromagnetic behavior of the composites. The average size of Fe_3O_4–CLPANI nanocomposites with core–shell structure was about 40 nm, and polydisperse. The results of TG, IR and UV spectra indicated that the Fe_3O_4 particles could improve the composite thermal stability due to interaction between the Fe_3O_4 particles and CLPANI polymer backbone.

Keywords: Polyaniline; Ferromagnetic properties; Core–shell structure

1. Introduction

Organic materials possessing both conducting and ferromagnetic functions are extremely useful due to their unique properties and potential application as batteries, electrochemical display devices, molecular electronic, non-linear optics, sensor, electrical-magnetic shields and wave-absorbing materials [1–6]. Bidan et al. [7] had reported an electrochemical method to prepare polypyrrole composite exhibiting the magnetic and conducting properties. Liu et al. [8] also prepared Fe_3O_4–polypyrrole composite. Recently, polyaniline (PANI) has attracted much attention because of its several unique properties. It is highly stable in air and soluble in various solvents, and exhibits dramatic changes in its electronic structure and physical properties at protonated state. It also shows ferromagnetic properties due to its high spin density [9]. Preparation of PANI with ferromagnetic properties has been mostly studied by Wan's group by two approaches. (1) Blending the PANI in *N*-methyl-2-pyrrolidone (NMP) with iron(II) sulfate aqueous solution, and precipitating Fe^{2+} into maghemite [10]. A poly(aniline-*co*-aminobenzenesulfonic acid (PAOABSA) copolymer containing γ-Fe_2O_3 magnetic particles has also been prepared by this approach [11]. (2) $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ are used as oxidants to react with aniline, followed by treatment with KOH aqueous [12].

Although Fe_2O_3–PANI composites have been successfully prepared by the above two approaches, the composites have low room temperature conductivity (10^{-4}–10^{-1} S/cm) and coercive force ($H_c = 0$). Their structures and properties are difficult to control due to synthetic method. Thus, further development of synthetic methods to produce novel electrical-magnetic composite with high room temperature conductivity and coercive force is highly desirable. Wrapping the Fe_3O_4 particles with PANI may generate novel nanomaterials with core–shell structure, intriguing electronic and magnetic properties.

Recently, a nanocomposite of Fe_3O_4–PANI with core–shell structure was prepared in our laboratory. But the Fe_3O_4 as a core was lost when the composites were soaked in 3 M

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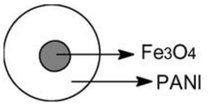


Scheme 1. The structure of Fe_3O_4–CLPANI nanocomposite.

H_2SO_4 aqueous due to the incoherence in structure of PANI, which is the cause of the difficulty to dope the PANI of composite. In this paper, we present a novel approach to synthesize a core–shell Fe_3O_4–cross-linked polyaniline (CLPANI) nanocomposite, where Fe_3O_4 is the magnetic core, and cross-linked PANI is the conductive shell. It can be doped in strong acid aqueous. The structure of the designed particles is shown in Scheme 1. The Fe_3O_4 nanoparticles were primarily prepared by precipitation–oxidation method, and the Fe_3O_4–CLPANI nanocomposites with core–shell structure were then synthesized via an in situ polymerization of aniline monomer and AFC in an aqueous, which contains a dispersion of Fe_3O_4 nanoparticles. The effect of iron oxide content in the composite with respect to the electrical and ferromagnetic properties of PANI composite has been investigated. The origin of their electrical and ferromagnetic properties is also discussed based on the structural characterization including elemental analysis, transmission electron micrograph (TEM), Fourier transform infrared (FTIR), UV spectrum (UV), X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

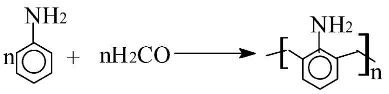
2. Experimental section

2.1. Materials

Aniline monomer (reagent grade, Fisher) was distilled under reduced pressure and stored below 0 °C. All the other reagents were analytical grade, and used without further purification, including polyethylene glycol (PEG $Mw = 4000$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), ammonia persulfate (APS), formaldehyde, sodium hydrate (NaOH), HCl (37%), hydrogen peroxide (H_2O_2, 30%) and ethanol, etc. Water was double distilled and bubbled for 30 min with N_2.

2.2. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 magnetic fluid was prepared by precipitation–oxidation method as follows: a mixture of 70.0 g of PEG ($Mw = 4000$) and 3.0 g of $FeSO_4 \cdot 7H_2O$ dissolved in 140 ml of distilled water was placed in a 250 ml four-necked round-bottom flask equipped with a condenser, a nitrogen inlet and a mechanical stirrer. The mixture was stirred under nitrogen for 30 min, followed by the addition of 20 ml of an aqueous solution containing 0.6 ml 40% H_2O_2. The reaction was allowed to proceed for 6 h at 50 °C at pH 13. The pH of reaction mixture was regulated with 3 M NaOH solution. The resulting magnetic fluid was dialyzed and purified repeatedly by magnetic field separation, decantation, and redispersed in water.



Scheme 2. Synthesis of AFC condensate.

2.3. Preparation of aniline–formaldehyde condensates

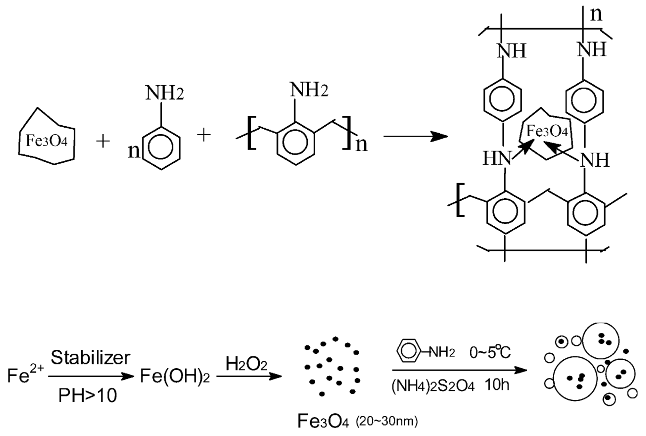
Aniline–formaldehyde condensate (AFC) was prepared by reacting formaldehyde with aniline as described in the literature [12]. In a 100 ml three-necked flask equipped with a stirrer, a condenser and an inlet of nitrogen, 25 ml of 37% formaldehyde was added to a mixture of 46.5 g of aniline and 15 ml of 37% HCl. Condensation was carried out at 100 °C for 2 h. The temperature was then decreased to 60 °C, then 20 ml of 30% NaOH added, resulting in insoluble liquid resin. The resin was washed with warm water three times and separated from the aqueous layer. The resin was kept at 80 °C under a reduced pressure of 10 kPa for 12 h to remove any unreacted aniline or formaldehyde. The condensation and the chemical structure of Fe_3O_4–CLPANI are shown in Scheme 2.

2.4. Synthesis of Fe_3O_4–cross-linked PANI nanocomposites with core–shell structure

Fe_3O_4–CLPANI magnetic particles were prepared via an in situ emulsion polymerization in aqueous solution containing Fe_3O_4 magnetic fluid and PEG. The polymerization was carried out in a 250 ml round-bottomed four-necked flask equipped with a mechanical stirrer, an inlet of nitrogen and a condenser. After the required amount of ingredients were placed into the flask, the polymerization was allowed to proceed for 12 h at 0–5 °C under stirring. The products were dialyzed and purified by magnetic field separation and decantation. This purification procedure was repeated for four times. The micropores were then immersed in a 0.1 M of HCl solution for 48 h. Non-encapsulated Fe_3O_4 powder was removed by repeated magnetic separation and washing with distilled water for three times. The products were dried under vacuum at 80 °C for 24 h. The synthesis procedure for Fe_3O_4 nanoparticles and Fe_3O_4–CLPANI composites is shown in Scheme 3.

2.5. Characterization

The UV–visible spectra were obtained on a UV-3000 spectrophotometer (Japan). The infrared (IR) spectra of all samples were recorded on a Nicolet 200SXV Fourier transform infrared (FTIR) using KBr pellets. The element analysis (C, H and N) was performed on a Carlo Erba 1106 elemental analyzer, and iron content was determined using an ICA900 (N + M) plasma spegraphoto. The morphology of the particles was studied with a Hillachi 600 transmission electron microscopy (TEM). The thermal gravitation was performed on a Perkin–Elmer TGA7. The XRD diagrams were obtained with a Miscience NH18XHF diffractometer



Scheme 3. Synthesis of magnetic and conducting polymer micropores.

using Fe Kα radiation. The conductivity of CLPANI composite powder at room temperature was measured with a programmable DC voltage–current detector on pressed pellets of composites under 20 MPa. The room temperature magnetization in the applied magnetic field was performed by model 155 vibrating sample magnetometer.

3. Results and discussion

3.1. Electrical properties

Coating experiments were carried out in 250 ml round-bottom flask according to the conditions described in Table 1. Fe_3O_4 content was found to affect significantly the conductivity of the resulting CLPANI composites as shown in Table 1. When 1.75% of Fe_3O_4 was incorporated into PANI, the conductivity was greatly reduced from 8.26×10^{-2} of pure CLPANI to 2.21×10^{-2} S/cm. Further increase of Fe_3O_4 content from 2.17 to 11.8% results in slight reduction of the conductivity at room temperature. The decrease in conductivity of Fe_3O_4–CLPANI composite with increasing Fe_3O_4 content was due to a decrease in the doping degree, assigned as a S/N ratio, the S/N ratios decrease from 0.29 to 0.09 with increasing Fe_3O_4 content from 0 to 11.8%. This was confirmed by elemental analysis results as shown in Table 1. The decrease of room temperature conductivity of Fe_3O_4–CLPANI composites may be attributed to two factors: (1) the insulting behavior of the iron oxide in the core of the nanoparticles, (2) a decrease of the doping degree. We believe that the latter factor plays a more important role in the conductivity of the composite.

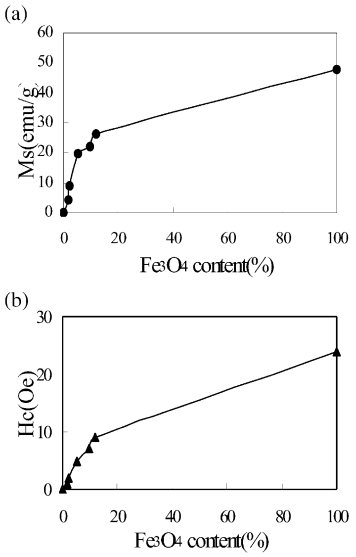


Fig. 1. (a) The M_s of composite depend on Fe_3O_4 content. (b) The H_c of composite depend on Fe_3O_4 content.

3.2. Magnetic properties

The magnetic properties of the composites depend on the Fe_3O_4 content as shown in Fig. 1. Increasing the Fe_3O_4 content from 0 to 11.8% considerably increases both the saturated magnetization (M_s) and the coercive force (H_c) from 0 to 26.34 emu/g and 0–9 Oe, respectively. Even if the Fe_3O_4 content is 11%, the value of M_s and H_c of the composite are increased greatly. Temperature dependence of the magnetization of CLPANI composite of the applied magnetic field of 10,000 Oe at temperatures between 24 and 500 °C was measured as shown in Fig. 2.

3.3. Structure characterization of Fe_3O_4–CLPANI composite

The morphology, average size distribution of magnetic

Table 1

Preparation conditions and the conductivity of Fe_3O_4–CLPANI composite (aniline: 4 ml; PEG: 20 ml (20% aqueous); APS: 5.0 g; ethanol: 20 ml; AFC: 0.05 g; reaction temperature: 0–5 °C, reaction time: 12 h)

Sample no.	Fe_3O_4 (2%, ml)	H_2O (ml)	Element content (%)			N/S ratio	Fe_3O_4 content (%)	Conductivity ($\times 10^{-2}$ S/m)
			C	H	N			
1	–	56				0.29	–	8.26
2	2	54	59.89	6.1	8.79	0.18	1.75	2.21
3	5	51	56.23	6.3	6.83	0.16	2.17	1.35
4	10	46	55.51	6.14	6.56	0.13	5.23	1.14
5	15	31	43.26	5.37	4.05	0.11	9.76	1.02
6	30	26	38.97	3.05	6.37	0.09	11.8	0.92

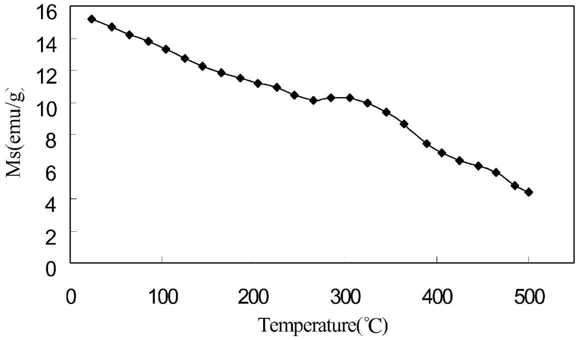


Fig. 2. Temperature dependence of the magnetization of sample 3 at the applied magnetic field of 10,000 Oe.

Fe_3O_4 nanoparticles was determined by a TEM. Fig. 1a shows the TEM micrograph of the Fe_3O_4 nanoparticles. The particles are almost spherical with diameters of about 10 nm. These particles are polydisperse, and some of them form multiparticle aggregates because of the magneto-dipole interparticle interactions. Fig. 1b shows the TEM micrographs of Fe_3O_4–CLPANI nanocomposite, which is quite polydispersed. About 80–90% of the particles are ranged from 30 to 40 nm. In order to identify the core–shell structure of nanoparticles, the composite was dissolved with NMP, which is a good solvent for PANI, and observed by TEM again. The micrograph was similar to the micrograph of Fe_3O_4 particles, shown as Fig. 1c. This indicated the Fe_3O_4–CLPANI nanocomposite was core–shell structure. The core is Fe_3O_4 nanoparticles and the shell is composed of CLPANI, whose cross-linked density is low enough to dissolve in NMP (Fig. 3).

Fig. 4 shows the XRD patterns of the Fe_3O_4–CLPANI nanocomposites, as well as the Fe_3O_4 nanoparticles. The main peaks are at $2\theta = 30.09$, 35.42, 43.05, 56.94, and 62.51°, which are in agreement with the XRD peaks of pure Fe_3O_4 observed in the CLPANI composite. This indicated that the Fe_3O_4–CLPANI nanocomposite contains Fe_3O_4 particles. According to Scherrer's equation [13]

$$\beta = \kappa\lambda/D\cos\theta$$

where λ is the X-ray wavelength, κ, the shape factor, D, the average diameter of the crystals in angstroms, θ, the Bragg angle in degree, and β is the line broadening measured by half-height in radium. The value of β depends on several factors, including the miller index of the reflecting plane and the shape of the crystal. If the shape is unknown β is often assigned a value of 0.89. When the reflecting peak at $2\theta = 62.51°$ is chosen to calculate the average diameter, the average sizes of the Fe_3O_4 particles are ranged between 10 and 12 nm, which is consistent with the results of TEM.

The TG results of nanocomposites show that the Fe_3O_4 particles can improve the thermal stability of the CLPANI nanocomposite shown in Fig. 5. The TG was preformed under a nitrogen atmosphere to minimize mass increase

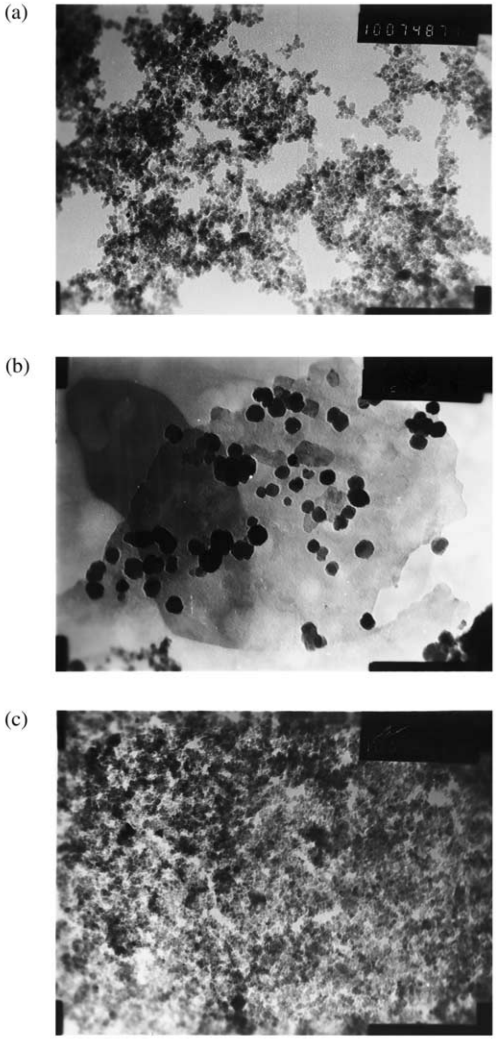


Fig. 3. The TEM photographs of Fe_3O_4 particles and Fe_3O_4–CLPANI composite: (a) Fe_3O_4; (b) Fe_3O_4–CLPANI; (c) Fe_3O_4 separated from Fe_3O_4–CLPANI composite.

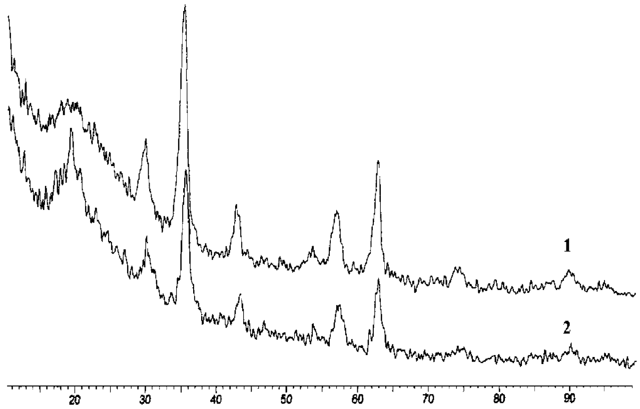


Fig. 4. XRD patterns of (1) −5.23% Fe_3O_4 in Fe_3O_4–CLPANI composite and (2) −9.76% Fe_3O_4 in Fe_3O_4–CLPANI composite. Recorded on a power diffractometer (Philips PW1830) with Fe Kα radiation.

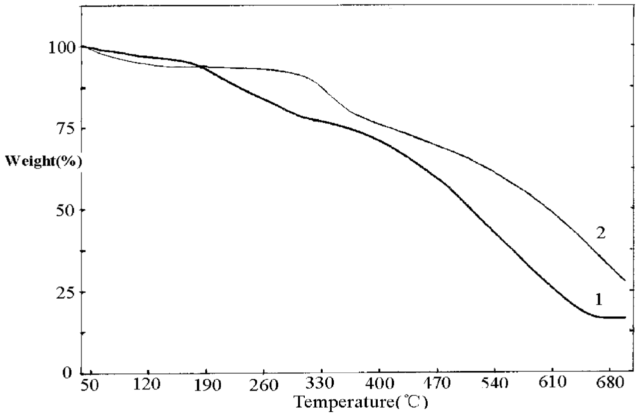


Fig. 5. The TG of CLPANI and Fe_3O_4–CLPANI nanocomposite: (1) CLPANI and (2) CLPANI composite with 5.23% Fe_3O_4.

due to iron oxidation, while allowing the CLPANI to thermally decompose almost completely. The pure CLPANI was decomposed at 430 °C, while the composites with 5.23% Fe_3O_4 particles were decomposed at 562 °C. The results of UV spectrum were shown in Fig. 6. The peak of composite with 2% Fe_3O_4 particles has a red shift of about 10 nm than that of parent CLPANI. The peak of parent CLPANI around 338 nm is based on the π–π^* transition of the phenyl ring, where the peak of Fe_3O_4–CLPANI is at 348 nm. These results indicated that there are some interactions between Fe_3O_4 particles and CLPANI. The FTIR spectra of the CLPANI and Fe_3O_4–CLPANI composite shown in Fig. 7 also support this conclusion. The characteristic absorption band of CLPANI is 1606 cm^{-1} (N=Q=N) and 1181 cm^{-1} (C–N), while the absorption peaks of Fe_3O_4–CLPANI composite shifted are 1589 and 1145 cm^{-1}. The interactive mechanism may be the lonepair electrons of N atom in CLPANI chain interact with 3d orbit of Fe atom to form coordinate bond, which could reduce the energy level interval of phenyl ring. This caused the UV absorption band of composite to have a red shift and the IR peaks a shift to lower wavenumber. Unfortunately, it is difficult to study the interaction between these two components. Thus, little is known about the microscopic interaction between the polymer and the Fe_3O_4 particles. The study of the interaction between the Fe_3O_4 particles and CLPANI polymer is now in progress.

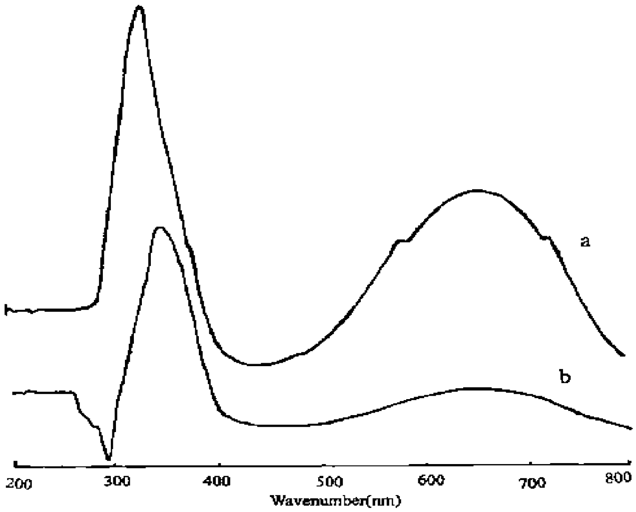


Fig. 6. The UV spectrum of CLPANI and Fe_3O_4–CLPANI nanocomposite: (a) CLPANI and (b) Fe_3O_4–CLPANI.

Fig. 7. IR spectra of CLPANI and Fe_3O_4–CLPANI composite: (1) CLPANI, (2) and (3) Fe_3O_4–CLPANI.

4. Conclusion

The resulting Fe_3O_4–CLPANI composites with core–shell structure showed ferromagnetic and electric properties. The saturated magnetization increased with an increase of Fe content. The conductivity depends on the Fe content and the doping degree. Structure characterization of the CLPANI composites proved that the magnetic particles were 20–30 nm in diameter, which was responsible for the ferromagnetic properties of the low coercive force, observed form the CLPANI composites. The TG, IR and UV characterization indicated that the Fe_3O_4 particles could improve the thermal stability of Fe_3O_4–CLPANI composites due to some interaction between the Fe_3O_4 particles and the CLPANI. Further investigation is now in progress.

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