

SYNTHESIS, CHARACTERIZATION AND THERMAL ANALYSIS OF POLYANILINE (PANI)/Co₃O₄ COMPOSITES

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Conducting polyaniline/Cobaltic oxide (PANI/Co₃O₄) composites were synthesized for the first time, by in situ deposition technique in the presence of hydrochloric acid (HCl) as a dopant by adding the fine grade powder (an average particle size of approximately 80 nm) of Co₃O₄ into the polymerization reaction mixture of aniline. The composites obtained were characterized by infrared spectra (IR) and X-ray diffraction (XRD). The composition and the thermal stability of the composites were investigated by TG-DTG. The results suggest that the thermal stability of the composites is higher than that of the pure PANI. The improvement in the thermal stability for the composites is attributed to the interaction between PANI and nano-Co₃O₄.

Keywords: composites, nanodimensional Co₃O₄, polyaniline, thermal stability

Introduction

Conducting polymer composites is some suitable composition of a conducting polymer with one or more inorganic nanoparticles so that their desirable properties are combined successfully. Over the last few years, conducting polymer composites have been studied with growing interest because of their numerous applications in various electrical and electronic devices [1–3]. The conducting polyaniline (PANI) is one of the promising conducting polymers due to its high conductivity, easy preparation, good environmental stability, and large variety of applications. Nowadays, the PANI has been successfully utilized in preparation of different composites, such as PANI/TiO₂, PANI/Fe₂O₃, PANI/ZrO₂ and PANI/polyethylene [4–7]. However, to the best of our knowledge, no publications have been found in literature about the preparation and the thermal stability of PANI/Co₃O₄ composites.

In this paper, we report the easy chemical synthesis of PANI/Co₃O₄ composites by in situ polymerization in the presence of hydrochloric acid (HCl) as a dopant. The composites obtained are characterized by infrared spectra (IR) and X-ray diffraction (XRD). The composition and thermal stability of PANI/Co₃O₄ composites have been investigated.

Experimental

Materials and methods

Aniline was obtained from Shengyang Federation Reagent Factory. Ammonium persulfate ((NH₄)₂S₂O₈,

APS) was purchased from Tianjing Bodi Chemical Co. whereas HCl was provided by Harbin Chemical Reagent Co. Co₃O₄ powder, in the form of fine particle (an average particle size of approximately 80 nm) was obtained by Nanjing High Technology Nano-Co. Ltd. All the chemical and reagents were used as received without further purification.

The PANI/Co₃O₄ composites were synthesized by in situ polymerization in the presence of Co₃O₄ nanoparticles and HCl as the dopant. A typical preparation process for PANI/Co₃O₄ composites was as follows: 1.6 mL aniline was injected to the dispersion of 50 mL of 2 M HCl containing Co₃O₄ nanoparticles under ultrasonic action to reduce the aggregation of Co₃O₄ nanoparticles. After 30 min, 4.56 g APS (dissolved in 50 mL de-ionized water) was dropped into the solution with constant stirring. The resulting mixture was allowed to react for 10 h at room temperature. The precipitated powder was filtered and washed with dilute HCl and de-ionized water to remove the unreacted aniline monomer and by-products. The product was dried in vacuum at 60°C for 24 h. Throughout the experiment, the molar ratio of aniline to HCl was 1:0.5 and the molar ratio of aniline to APS was retained at 1:1. Only the amount of Co₃O₄ was changed to investigate the effect of the Co₃O₄ nanoparticles on the composition, thermal stability and conductivity of PANI/Co₃O₄ composites.

Infrared absorption spectroscopy spectra (IR) were measured on an IR spectrophotometer (Bruck Equinox 55) using the KBr pellet technique to determine the structure of the pure PANI and PANI/Co₃O₄ composites. The X-ray scattering patterns of Co₃O₄,

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the pure PANI and PANI/Co₃O₄ composites were recorded on an X-ray diffraction instrument (Rigaku Miniflex). TG-DTG measurements of the samples were carried out with a Setsys 16/18 thermogravimetric analyzer (Setaram Co., France) from room temperature to 800°C in air at a heating rate of 10°C min⁻¹.

Results and discussion

Infrared spectra analysis (IR)

The IR spectra of the pure PANI and PANI/Co₃O₄ composites are shown in Fig. 1. The main characteristic peaks of the pure PANI (Fig. 1a) are assigned as follows: 1489 and 1562 cm⁻¹ are attributed to C–C stretching of the benzenoid and quinoid rings, respectively, for the HCl doped PANI. The characteristic absorption band around 1244 cm⁻¹, which is related to the C–N stretching in bipolaron structure, can be observed [8]. These results indicate that the pure PANI is highly doped and exists in conducting emeraldine salt form. The peak at 1299 cm⁻¹ corresponding to C–N stretching of secondary amine in polymer main chain can be clearly seen. The existence of absorption band at 1122 cm⁻¹ has been interpreted as origination from plane bending vibration of C–H, which is formed in the structure of B–N⁺H–Cl, Q=N⁺H–Cl and N=Q=N during the protonation of HCl-doped PANI [9]. For the PANI/Co₃O₄ composites (Fig. 1b), its IR spectrum is almost identical to that of the pure PANI. But all bands shift slightly towards red, and the intensity ratio of quinonoid to benzenoid band has also changed. These results indicate that some interactions exist between PANI and nano-Co₃O₄.

X-ray diffraction analysis (XRD)

Figure 2 shows the X-ray diffraction patterns of the pure PANI, PANI/Co₃O₄ composites as well as Co₃O₄

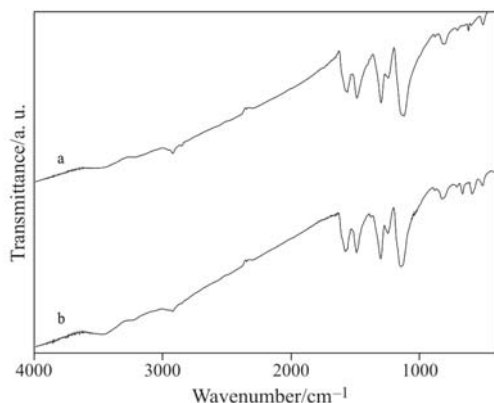


Fig. 1 IR spectra of the pure a – PANI and b – PANI/Co₃O₄ composites

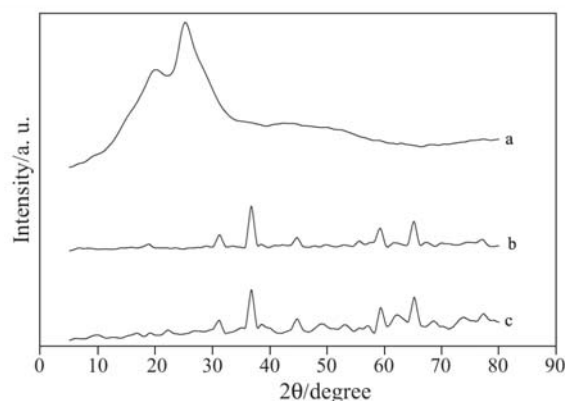


Fig. 2 X-ray scattering patterns for a – pure PANI, b – PANI/Co₃O₄ composite and c – Co₃O₄ nanoparticles

nanoparticles. The pure PANI powder (Fig. 2a) exhibits two broad peaks at 2θ angles around 20 and 26°, which indicates the PANI has some degree of crystallinity. These peaks may be assigned to the scattering from PANI chains at interplanar spacing [10]. When the Co₃O₄ nanoparticles are incorporated into PANI, the broad diffraction peaks of the PANI disappear gradually, which is possibly because the nanoparticles have acted as ‘impurities’ to hamper the growth of the PANI ‘crystallites’ [11]. A few new reflection peaks appear in the XRD diagram of the composite (Fig. 2b). The Co₃O₄ nanoparticles display several relatively strong reflections peaks (Fig. 2c) in the 2θ region of 5–80°, and it thus becomes clear that the peaks of the composites in the corresponding 2θ angles are the Bragg reflections of the Co₃O₄ nanoparticles.

The composition analysis

The composition of PANI/Co₃O₄ composites can be analyzed from TG data [12–14]. Table 1 gives the experimental values and the expected values of the PANI loading per gram of the composite. Here, we assume a constant yield of polymerization (1.7 g) as obtained in the pure PANI (i.e., without addition of Co₃O₄) synthesized under the same conditions. From Table 1, it can be seen that the percent of the PANI loading per gram of the composite shows a tendency to fall with increasing Co₃O₄ amount. Comparing the expected values with those obtained actually from TG analysis, it suggests that the PANI content is higher when the amount of Co₃O₄ ≥ 0.3 g. This demonstrates that the presence of Co₃O₄ increases the yield of the PANI, which can be explained on the basis of the surface adsorption of the aniline monomer and subsequent polymerization on the Co₃O₄ surface. The adsorption of aniline on different surfaces and subsequent formation of PANI has been reported

Table 1 The characteristics of PANI/Co₃O₄ composites

Sample No.	Amount of Co ₃ O ₄ /g	PANI/% g ⁻¹ _{composites}		T _i /°C
		observed	expected	
PANI	0.0	100	100.0	321
PANI/Co ₃ O ₄ -a	0.1	92	94.4	326
PANI/Co ₃ O ₄ -b	0.3	85	85.0	329
PANI/Co ₃ O ₄ -c	0.5	78	77.2	342
PANI/Co ₃ O ₄ -d	0.7	72	70.8	337
PANI/Co ₃ O ₄ -e	0.9	67	65.4	334

*T_i stands for the temperature at which decomposition starts

in [15, 16]. Similar processes might take place in the presence of Co₃O₄ particles with a high surface area.

Thermogravimetric analysis (TG)

The thermal stability of the composites is analyzed from TG-DTG data. Figure 3 represents the TG-DTG curves of the pure PANI and Co₃O₄ particles. From this figure, it can be seen that Co₃O₄ nanoparticles is very stable in air and has not any transition in the temperature range of 30–800°C. The pure PANI shows two-step mass loss process, which is similar to the observation by Gupta and Umare [17] and Khor *et al.* [18]. The first step occurs in the range 63–143°C, which is attributed to the expulsion of water and dopant (HCl) from the matrix of the PANI. The second-step mass loss occurs between 321 and 695°C, which is due to the degradation of the PANI chain. Figure 4 gives the TG curves of PANI/Co₃O₄ composites. Curves a–e correspond to the amount of Co₃O₄ added as 0.1, 0.3, 0.5, 0.7 and 0.9 g, respectively. Figure 4 shows that the trend of degradation of PANI/Co₃O₄ composites is similar to that of the pure PANI but thermal stability of the composites has changed. T_i (the temperature at which decomposition starts) is a criterion to indicate the thermal stability of the materials. The larger the value of T_i, the higher the thermal stabil-

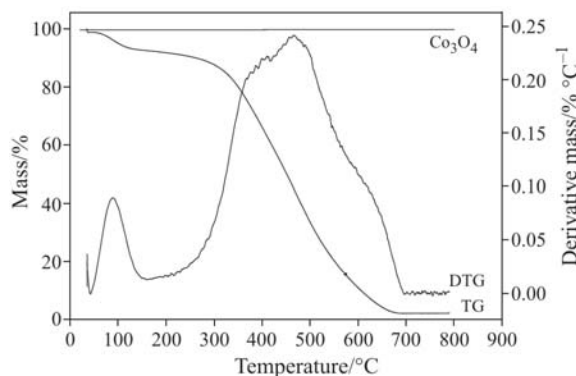


Fig. 3 TG-DTG curves of the pure PANI and Co₃O₄ nanoparticles

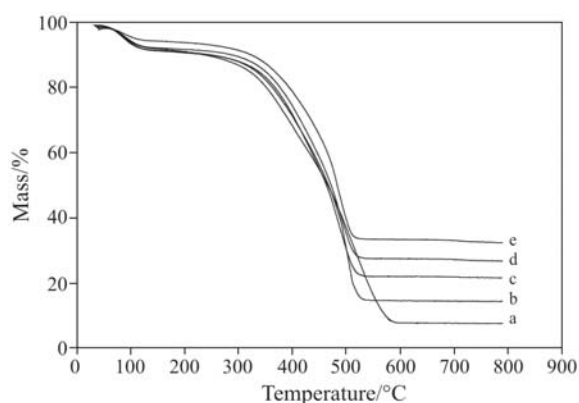


Fig. 4 TG curves of PANI/Co₃O₄ composites. Curves a–e correspond to the amount of Co₃O₄ (0.1, 0.3, 0.5, 0.7 and 0.9 g) in the composite

ity is. T_i values of the pure PANI and PANI/Co₃O₄ composites are listed in Table 1. From Table 1, it can be seen that the thermal stability of PANI/Co₃O₄ composites is higher than that of the pure PANI, which indicates that some interaction exists between Co₃O₄ nanoparticles and PANI backbone. It also can be seen from Table 1 that the thermal stability PANI/Co₃O₄ composites shows a tendency to first increase and then decrease with increasing Co₃O₄ amount. When the mass ratio of PANI to Co₃O₄ is 78 to 22, the thermal stability of the composite is the highest.

Conclusions

We successfully synthesized polyaniline (PANI) composites containing Co₃O₄ nanoparticles (about 80 nm in diameter) by 'in situ' polymerization in the presence of hydrochloric acid (HCl) as the dopant. IR spectra and XRD pattern indicate that some interaction exists between PANI and nano-Co₃O₄. TG analysis suggests that the thermal stability of PANI/Co₃O₄ composites is higher than that of the pure PANI. This enhanced thermal stability of the composites is also ascribed to the interaction between PANI and nano-Co₃O₄.

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