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Synthesis, characterization and thermal analysis of polyaniline/ZrO_2 composites

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Abstract

Conducting polyaniline–zirconium dioxide (PANI/ZrO_2) composites were synthesized by 'in situ' deposition technique in the presence of hydrochloric acid (HCl) as dopant by adding the fine grade powder (average particle size of approximately 20 nm) of ZrO_2 into the polymerization reaction mixture of aniline. The composites obtained were characterized by infrared spectra (IR) and X-ray diffraction (XRD) and thermogravimetric analysis (TGA). TG curves and DTG curves of the composites suggest that the thermal degradation process of PANI/ZrO_2 composites proceeds in two-steps and the composites are more thermally stable than that of the pure PANI. The improvement in the thermal stability for the composites is attributed to the interaction between PANI and ZrO_2, which restricts the thermal motion of PANI chains and shields the degradation of PANI in the composites.

Keywords: Polyaniline; PANI/ZrO_2 composite; TGA; Thermal stability; Interaction

1. Introduction

The conducting polyaniline (PANI) is one of the promising conducting polymers due to the following reasons: (i) it can be synthesized easily, (ii) it is comparatively stable in air, (iii) it has high conductivity and (iv) it shows large variety of applications such as in electrochromic devices, light-emitting diodes, chromatography, secondary batteries, electrostatic discharge protection, and corrosion-protecting paint [1]. Nowadays, conducting polymer composites have received great attention because of their unique properties and promising potential applications in electrical devices [2–4]. Therefore, the preparation of PANI composites has been the subject of considerable interest recently. Many papers on PANI/inorganic composites such as PANI/TiO_2, PANI/Fe_3O_4, and PANI/MnO_2 have been published in the literature [5–7]. However, to the best of our knowledge, no works have been reported on the preparation of PANI/ZrO_2 composites by 'in situ' polymerization.

Knowledge of thermal stability and degradation behaviors is useful to modify the polymers for newer application. Several studies have been made on the thermal stability of PANI salts by TGA and DTA [8–12]. Two forms of thermal behaviors of polyaniline salts are reported in these literatures. The one form indicates a two-step weight loss process in which, initially, water escapes from the polymer chains, followed by thermal degradation of the polymer salts. The other form shows a three-step weight loss process wherein water escapes first, followed by acid dopant present in the polymer salt, and finally completed degradation of the polymer salts. However, for the PANI/ZrO_2 composites prepared by 'in situ' polymerization, survey of the literature reveals that thermal stability and degradation behaviors of PANI/ZrO_2 composites have not been studied.

In the present work, we report the easy chemical synthesis of PANI/ZrO_2 composites by 'in situ' polymerization in the presence of hydrochloric acid (HCl) as a dopant. The com-

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posites obtained were characterized by infrared spectra (IR) and X-ray diffraction (XRD). The thermal stability and degradation behaviors of the composites were studied by thermal gravimetric analysis (TGA).

2. Experimental

2.1. Materials

Aniline was obtained from Shengyang Federation Reagent Factory. Ammonium persulfate ($(NH_4)_2S_2O_8$, APS) was purchased from Tianjing Bodi Chemical Co. whereas hydrochloric acid (HCl) was provided by Haerbin Chemical Reagent Co. ZrO_2 powder, in the form of fine particle (average particle size of approximately 20 nm) was obtained by Nanjing High Technology Nano-Co. Ltd. All the chemical and reagents were used as received without further purification.

2.2. Synthesis of PANI/ZrO_2 composites

The PANI/ZrO_2 composites were synthesized by 'in situ' polymerization in the presence of ZrO_2 nanoparticles and HCl as the dopant. A typical preparation process for PANI/ZrO_2 composites was as follows: 1.6 ml aniline was injected to the dispersion of 50 ml of 2 M HCl containing ZrO_2 nanoparticles under ultrasonic action to reduce the aggregation of ZrO_2 nanoparticles. After 30 min, 4.56 g APS (dissolved in 50 ml de-ionized water) was dropped into the above dispersion with constant stirring. The resulting mixture was allowed to react for 10 h at room temperature. The precipitated powder was filtered and washed with 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. For each experiment, the molar ratios of aniline to HCl and to APS for either the pure PANI or PANI/ZrO_2 composites were retained at 1:0.5 and 1:1, respectively.

2.3. Characterization

Bruck Equinox 55 spectrophotometer was used to determine the infrared (IR) absorption spectra of the pure PANI and PANI/ZrO_2 composites in the wavelength range 4000–400 cm^{-1}. The X-ray scattering patterns of ZrO_2 for the pure PANI and PANI/ZrO_2 composites were recorded on an X-ray diffraction instrument (Rigaku Miniflex).

2.4. Thermal analysis

A thermogravimetric analyzer (Model: setsys 16/18, SETARAM France) was used for TG measurements of the samples from 30 to 900 °C in air at the heating rate of 10 °C/min. The weight of the sample used was 6.0 mg in all cases.

3. Results and discussion

3.1. Structure characterization of PANI/ZrO_2 composite

The IR spectra of the pure PANI and PANI/ZrO_2 composite 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 [13]. 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 [14]. For PANI/ZrO_2 composite (Fig. 1b), its IR spectrum is almost identical to that of the pure PANI. But all bands shift slightly, which indicates that some interaction exists between PANI and nano-ZrO_2.

Fig. 2 shows the X-ray diffraction patterns of the pure PANI, PANI/ZrO_2 composite as well as ZrO_2 nanoparticles. The pure PANI powders (Fig. 2a) exhibit two broad peaks at 2θ angles around 20° and 26°, which indicates the PANI has crystallinity to a certain extent. These peaks may be assigned to the scattering from PANI chains at interplanar spacing [15]. When ZrO_2 nanoparticles is incorporated into PANI, the broad diffraction peaks of the PANI become very weak. Therefore, diffraction pattern of the composite (Fig. 2b) is the same as nano-ZrO_2 (Fig. 2c), which means that PANI deposited on the surface of ZrO_2 has no effect on crystallization performance of nano-ZrO_2.

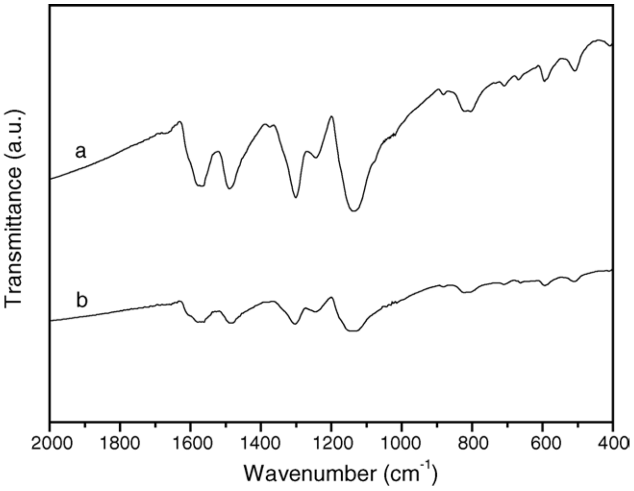

Fig. 1. IR spectra of the pure PANI (a) and PANI/ZrO_2 composite (73.7/26.3 (w/w)) (b).

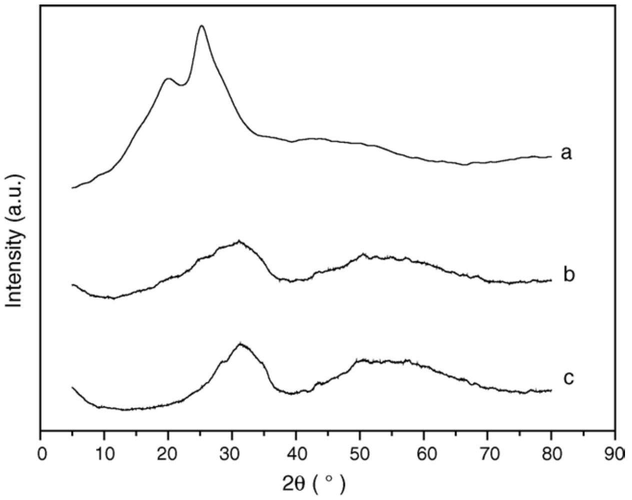

Fig. 2. X-ray scattering patterns for the pure PANI (a), PANI/ZrO_2 composite (73.7/26.3 (w/w)) (b) and ZrO_2 nanoparticles (c).

3.2. *Thermal analysis of PANI/ZrO_2 composite*

The composition of PANI/ZrO_2 composites can be analyzed from TGA. Fig. 3 shows the thermogravimetric curves (TG curves) and corresponding derivative curves (DTG curves) for a ZrO_2, a pure PANI and a PANI/ZrO_2 composite containing the amount of ZrO_2 (47.0 wt.%). TG curve of the PANI/ZrO_2 composite reveals a total loss of ca. 68.5% at ca. 560 °C, which remained constant till 900 °C. In contrast, the pure PANI shows a weight loss of ca. 97.9% while ZrO_2 reveals only a partial loss of volatile impurities of about 13.4% in the same temperature range. In the light of the reasoning put forward by Armes et al. [16] for PANI/SiO_2 system, these data implied that the polymer content per gram of the composite is $(68.5 - 13.4 - 2.1)\% = 53.0\%$ and the ZrO_2 content is $(100 - 53.0)\% = 47.0\%$.

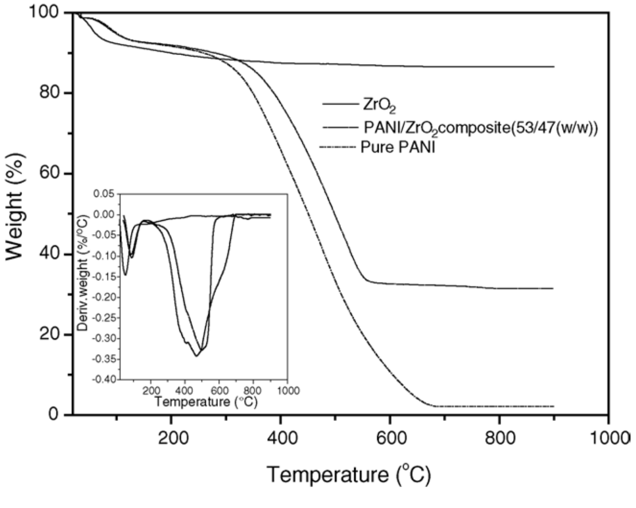

Fig. 3. TG curves and DTG curves (inset) of a ZrO_2, a pure PANI and a PANI/ZrO_2 composite (53.0/47.0 (w/w)).

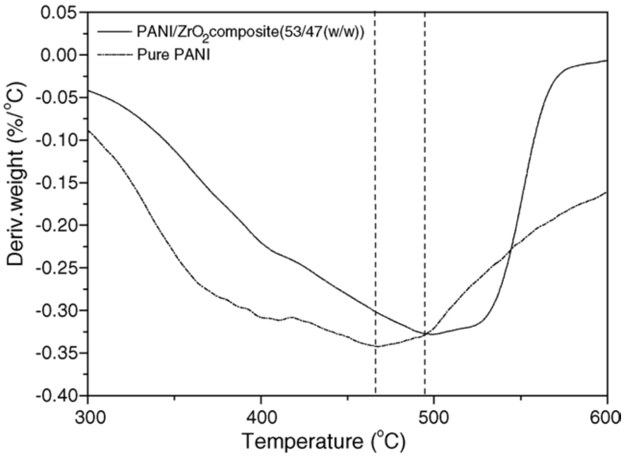

Fig. 4. DTG curves of pure PANI and PANI/ZrO_2 composite (53.0/47.0 (w/w)). The curves represent the magnification of the DTG curves (inset) shown in Fig. 3.

In Fig. 3, ZrO_2 shows one-step weight loss in the temperature ranges 30–900 °C, which is due to probable loss of water and volatile impurities. In general, the TG curve of the pure PANI shows two-step weight loss process. The first-step indicates a 8–9% weight loss at temperatures up to 120 °C. This step can be attributed to the expulsion of water molecule and the dopant (HCl) form PANI chains. The second-step weight loss occurs between 315 and 660 °C, which is due to the degradation of PANI chains. The interesting observation is that the DTG curve (inset) of the pure PANI corresponding to the second-step weight loss of the TG curve, show two minima rather than one minimum. The first minimum is due to the loss of low molecular weight polymer while the second minimum is the result of the degradation of high molecular weight polymer. The trend of degradation of the composite is similar to that of the pure PANI and also shows two-step weight loss process. In order to carefully compare the thermal behavior of the composite with that of the pure PANI, the DTG curves shown in the inset of Fig. 3 are enlarged in Fig. 4. Note that the temperature of pure PANI at the minimum of the DTG curve (T_I) is at 467.9 °C, but the minimum temperature in the case of the PANI/ZrO_2 composite is significantly shifted to a higher temperature by about 31 °C. This result suggests that the composite system is more thermally stable than the pure PANI, which would be explained by the fact that a strong interaction between PANI and ZrO_2 restricts thermal motion of the PANI in the composite and enhances thermal stability of the composite.

Fig. 5 shows the TG curves and corresponding DTG curves of PANI/ZrO_2 composites as a function of ZrO_2 content. As the amount of ZrO_2 content is increased, the total weight loss of the composite decreases (Fig. 5a). It is noticed from the DTG curves that T_I, represented by an arrow in Fig. 5b, moves to a lower temperature with increase of the ZrO_2 content in the composites. For the case of PANI/ZrO_2 composites, the relative shift of T_I with respect to the T_I for the pure PANI ($\Delta T_I = (T_{I,\text{composites}} - 467.9)/467.9$) was measured as a function of ZrO_2 content and is shown in Fig. 6. As the ZrO_2 content in the composite is increased, the relative shift of T_I sharply decreases and eventually approaches nearly zero, as indicated in the figure. The reason would be explained as follows: As the ZrO_2 content in the composite is increased, the interaction between ZrO_2 and PANI gradually weakened, which leads to the free PANI chains coexist in the PANI/ZrO_2 composites. Thus, the thermal decomposition of this system can occur in both confined and free states at the same time. However, the contribution from the free PANI chains may be more significant for thermal decomposition because these chains in the composites are more exposed to the heating when compared with the PANI chains interacted with ZrO_2. So the relative shift of T_I sharply decreases.

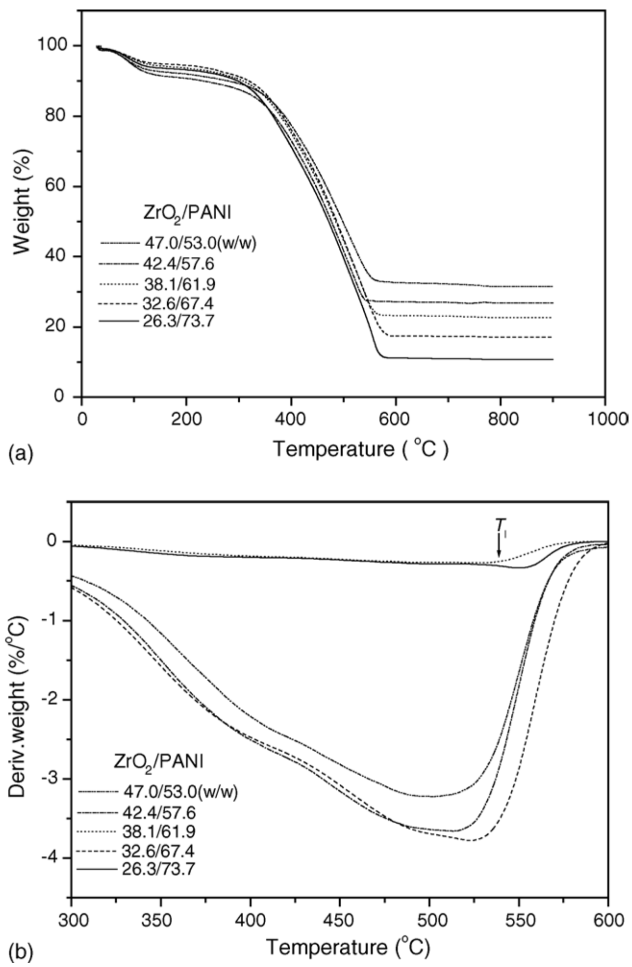

Fig. 5. (a) TG curves and (b) DTG curves of PANI/ZrO_2 composites with different amounts of ZrO_2 as a function of temperature.

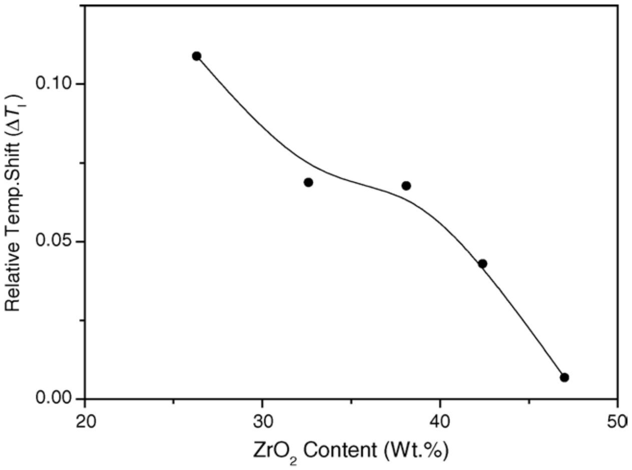

Fig. 6. Relative temperature shift (ΔT_I) of PANI/ZrO_2 composites as a function of ZrO_2 content in the composites.

4. Conclusions

The following conclusions can be drawn form the present investigation

1. We successfully synthesize polyaniline (PANI) composites containing ZrO_2 nanoparticles (about 20 nm in diameter) by 'in situ' polymerization in the presence of hydrochloric acid (HCl) as the dopant.
2. IR spectra and XRD pattern indicate that some interaction exists between PANI and nano-ZrO_2.
3. The PANI/ZrO_2 composites are found to be more thermally stable than that of the pure PANI. This enhanced thermal stability of the composites is ascribed to the interaction between PANI and nano-ZrO_2.

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