

Thermal stability of several polyaniline/rare earth oxide composites (I): polyaniline/CeO₂ composites

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Abstract Polyaniline (PANI)/CeO₂ composites were prepared by adding CeO₂ powder into the polymerization reaction mixture of aniline. Fourier transform infrared spectra (FTIR) and X-ray diffraction (XRD) were used to characterize the composites. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were used to study the thermal stability of the composites. IR and XRD results show that interaction exists between PANI and CeO₂. This interaction maybe is hydrogen bonding action between the hydroxyl groups on the surface of the CeO₂ and the imine groups in the PANI molecular chains. TG–DTG analysis indicates that the thermal stability of the composites is higher than that of the pure PANI. The improvement in the thermal stability of the composites is attributed to the interaction between PANI and CeO₂, which restricts the thermal motion of PANI chains and shields the degradation of PANI in the composites.

Keywords PANI/CeO₂ composite · Interaction · Thermal stability · TG–DTG

Introduction

Over the last few years, polyaniline (PANI) composites have been studied with growing interest because of their

numerous applications in various electrical and electronic devices. Many articles on PANI/inorganic composites such as PANI/TiO₂, PANI/Fe₃O₄, PANI/Fe₂O₃, PANI/MnO₂, PANI/ZrO₂, PANI/Co₃O₄, PANI/Al₂O₃, and PANI/NiO have been published in the literatures [1–8]. PANI usually combined with inorganic components to form composites to improve physical, mechanical, and electrical properties such as enhanced solubility, conductivity, magnetic, optoelectronic properties, etc. In recent years, rare earth oxides are gradually introduced to the area of PANI composites because of their excellent physical and chemical characteristics. Among those oxides, cerium dioxide (CeO₂) is becoming an important material in various fields of modern technology, such as catalysis, microelectronics, optoelectronics, electrochemical devices, ultraviolet blockers, etc. [9–11]. The reports about the synthesis of PANI/CeO₂ composite have been found [12, 13]. However, survey of the literature reveals that thermal stability and degradation behavior of the composite have not been studied.

Knowledge of thermal stability and degradation behaviors is useful to modify the polymer for newer application. Many studies have been made on the thermal stability of PANI salts by TGA and DTA [14–17]. Two forms of thermal behaviors of PANI salts are reported in these literatures. The one form indicates a two-step mass 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 mass loss process wherein water escapes first, followed by acid dopant present in the polymer salts, and finally completed degradation of the polymer salts. And several studies have also been made on the thermal stability of PANI/inorganic composite [5–8]. The results indicate that more thermally stable inorganic particles improve the thermal properties of PANI by the interaction between them. CeO₂ also has

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excellent thermal stability. Is it capable of improving the thermal stability of PANI? If it can, how could it?

In this study, we report the easy chemical synthesis of PANI/CeO₂ composites by 'in situ' polymerization in the presence of hydrochloric acid (HCl) as a dopant. The composites obtained were characterized by infrared spectra (IR) and X-ray diffraction (XRD). The thermal property of the composite was studied by thermogravimetry and derivative thermogravimetry (TG-DTG).

Experimental

Chemicals and materials

Aniline obtained from Shengyang Federation Reagent Factory was purified twice by vacuum distillation and was stored in refrigerator before use. Ammonium persulfate ((NH₄)₂S₂O₈, APS) was purchased from Tianjing Bodi Chemical Co. whereas HCl was provided by Haerbin Chemical Reagent Co. CeO₂ powder was obtained by Shanghai Tuelong Rare Earth New Materials Co. Ltd. All chemical reagents were of analytical grade.

Material preparation

The PANI/CeO₂ composites were synthesized by 'in situ' polymerization in the presence of CeO₂ particles and HCl as the dopant. A typical preparation process has been described in detail in our early work [5, 6]. 1.6 mL aniline was injected to the dispersion of 50 mL of 0.5 M HCl containing CeO₂ powder under ultrasonic action. 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 333 K for 24 h. For each experiment, the molar ratios of aniline to HCl and to APS for either the pure PANI or PANI/CeO₂ composites were retained at 1:0.5 and 1:1, respectively.

Methods of characterization

Bruck Tensor 27 spectrophotometer was used to determine the IR absorption spectra of the pure PANI and PANI/CeO₂ composites in the wavelength range 4000–400 cm⁻¹. The X-ray scattering patterns of CeO₂, PANI and PANI/CeO₂ composites were recorded on an X-ray diffraction instrument of FANG YUAN DX-2000.

Thermal analysis

The thermal stability of pure PANI, CeO₂, and PANI/CeO₂ composites were performed on a thermogravimetric analyzer (Model: HCT-1/2, HENGJIU China). All samples were heated from room temperature to 1100 K in air at a heating rate of 10 K min⁻¹. The mass of the samples used was 10.0 mg in all cases.

Results and discussion

Structure characterization of PANI/CeO₂ composites

The IR spectra of the pure PANI and PANI/CeO₂ composite are shown in Fig. 1. The main characteristic peaks of the pure PANI are assigned as follows: 1565 and 1494 cm⁻¹ are attributed to C=C stretching of the quinoid and benzenoid rings, respectively, for the HCl-doped PANI. The characteristic absorption band around 1245 cm⁻¹, which is related to the C–N stretching in bipolaron structure, can be observed [18]. These results indicate that the pure PANI is highly doped and exists in conducting emeraldine salt form. The peak at 1308 cm⁻¹ corresponding to C–N stretching of secondary amine in polymer main chain can be clearly seen. The existence of absorption band at 1152 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 [19]. Comparing to the corresponding peaks of pure PANI at 1308 and 1152 cm⁻¹, the peaks of the PANI/CeO₂

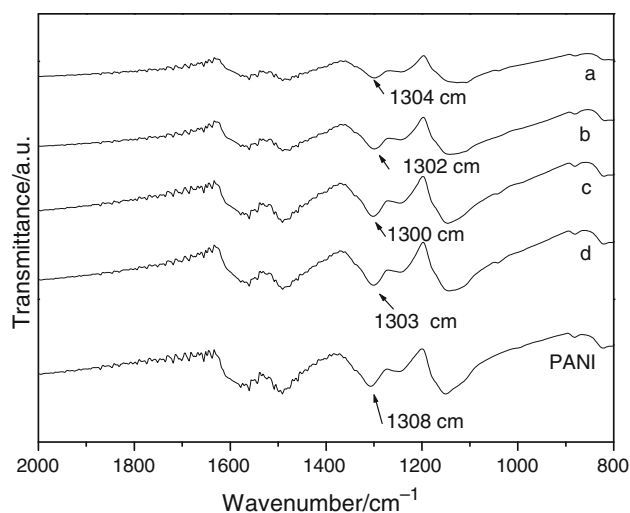


Fig. 1 IR spectra of pure PANI and PANI/CeO₂ composites. *a* PANI/CeO₂[86.8/13.2(W/W)]; *b* PANI/CeO₂ [83.4/16.6(W/W)]; *c* PANI/CeO₂[70.4/29.6(W/W)]; *d* PANI/CeO₂ [61.6/38.4(W/W)]

composite (Fig. 1a–d) shift slightly to lower wave numbers. This may be caused by the hydrogen bonding action between the hydroxyl groups on the surface of the CeO₂ ($\text{CeO}_2 + \text{H}_3\text{O}^+ = \text{Ce}^{4+} + \text{OH}^-$) and the imine groups in the PANI molecular chains. It is noticed from the IR spectra that the interaction between PANI and CeO₂ enhances first and then weakens when the CeO₂ content in the composites is higher than 70.4 wt%.

Figure 2 shows the X-ray diffraction patterns of the pure PANI, PANI/CeO₂ composites as well as CeO₂ powder. The pure PANI exhibits 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 [20]. As the CeO₂ content is increased in the composite, the broad diffraction peaks of the PANI become weak. And when the CeO₂ content amount to 70.4 wt%, diffraction pattern of the composite (Fig. 2c) is the almost same as CeO₂. The results suggest that the addition of CeO₂ impedes the crystallization of the PANI molecular chain. When PANI is absorbed on the surface of the CeO₂, the molecular chain of the absorbed PANI is confined, and the degree of crystallinity decreases [21]. The results also indicate that the interaction exists between PANI and CeO₂.

CeO₂ content in PANI/CeO₂ composites

CeO₂ content in PANI/CeO₂ composites can be calculated from TG curves of PANI/CeO₂ composites. Figure 3 shows TG curves of the pure PANI, CeO₂ as well as PANI/CeO₂ composites. The pure PANI shows a mass loss of ca. 99.1% from room temperature to 1100 K. In the same temperature,

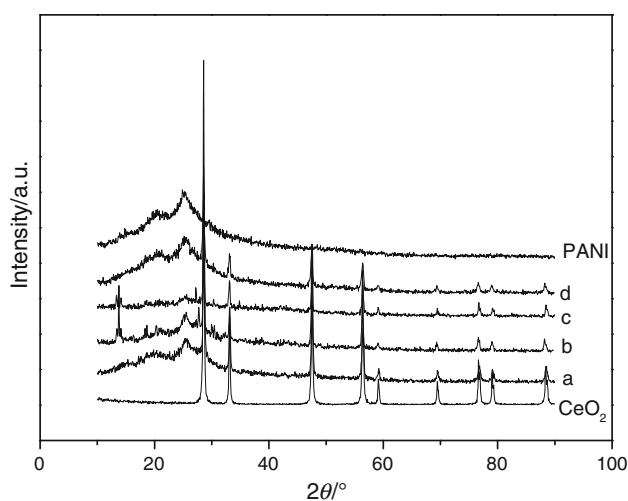


Fig. 2 X-ray scattering patterns for the pure PANI, CeO₂, and PANI/CeO₂ composites. *a* PANI/CeO₂[86.8/13.2(W/W)]; *b* PANI/CeO₂ [83.4/16.6(W/W)]; *c* PANI/CeO₂[70.4/29.6(W/W)]; *d* PANI/CeO₂ [61.6/38.4(W/W)]

the CeO₂ shows no mass loss. In contrast, TG curve of PANI/CeO₂ composite [70.4/29.6(mass/mass)] reveals a total loss of ca. 71.3%. In the light of our early research [5] for PANI/ZrO₂ system, these data implied that the polymer content per gram of the composite is (71.3–0.93) % = 70.4% and the CeO₂ content is (100–70.4) = 29.6%.

Thermal stability of PANI/CeO₂ composites

It can be seen from Fig. 3 that CeO₂ is very stable in air and has not any transition from the room temperature to 1100 K. The TG curve of the pure PANI shows two-step mass loss processes. The first-step mass loss can be attributed to the expulsion of water molecule and the dopant (HCl) from PANI chains. The second-step mass loss occurs between 548 and 913 K, which is due to the degradation of PANI chains. The trend of degradation of PANI/CeO₂ composite 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 stability is. T_i as a function of CeO₂ content is shown in Fig. 4. From Fig. 4, it can be seen that the thermal stability of PANI/CeO₂ composites is greatly higher than that of the pure PANI and shows a tendency to first increase and then decrease with increasing CeO₂ amount. When the mass ratio of PANI to CeO₂ is 70.4 to 29.6, the thermal stability of the composite is the highest. The reason would be explained as follows: As the CeO₂ content in the composite is increased, the interaction between CeO₂ and PANI strengthens, which reduces the amount of the free PANI chains in the composites. We think the contribution from the free PANI

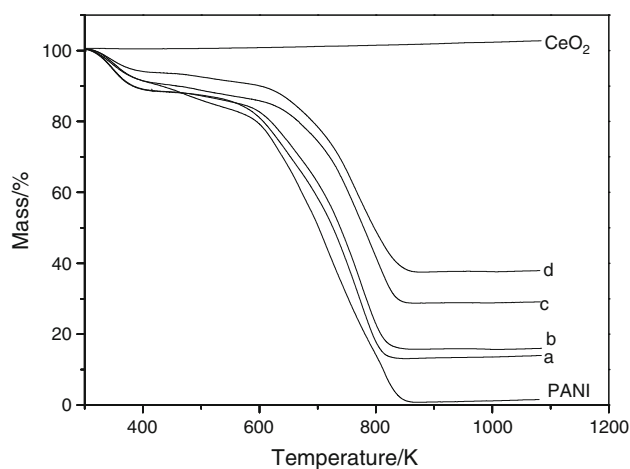


Fig. 3 TG curves of the pure PANI, CeO₂ as well as PANI/CeO₂ composites. *a* PANI/CeO₂[86.8/13.2(W/W)]; *b* PANI/CeO₂ [83.4/16.6(W/W)]; *c* PANI/CeO₂[70.4/29.6(W/W)]; *d* PANI/CeO₂ [61.6/38.4(W/W)]

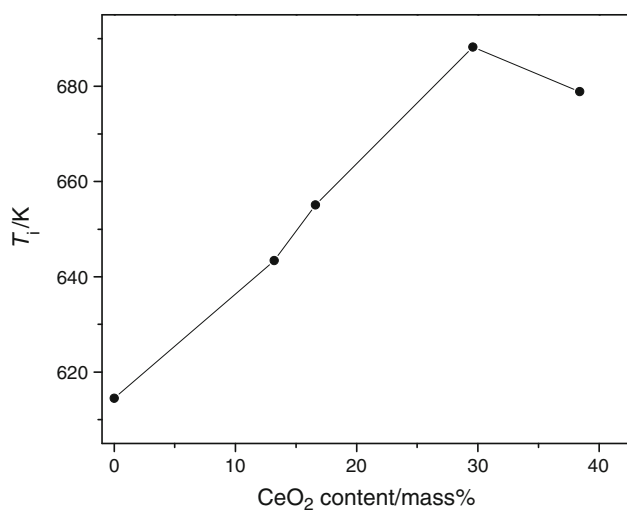


Fig. 4 The temperature at which decomposition starts (T_i) of PANI/CeO₂ composites as a function of CeO₂ content in the composites

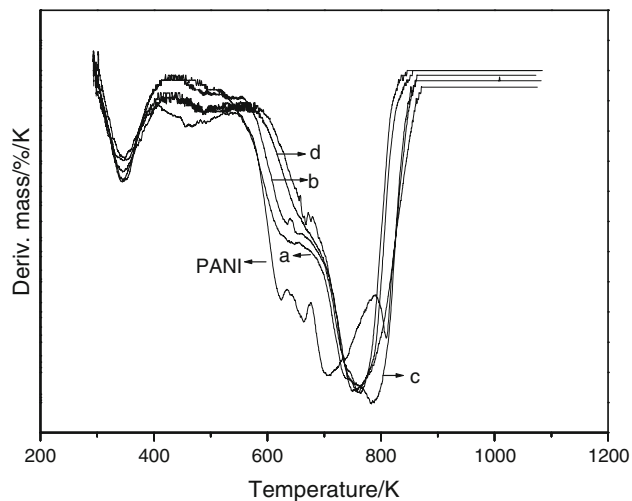


Fig. 5 DTG curves of the pure PANI and PANI/CeO₂ composites. *a* PANI/CeO₂[86.8/13.2(W/W)]; *b* PANI/CeO₂ [83.4/16.6(W/W)]; *c* PANI/CeO₂[70.4/29.6(W/W)]; *d* PANI/CeO₂ [61.6/38.4(W/W)]

chains may be more significant for thermal decomposition because these free chains are more exposed to the heating when compared with the PANI chains interacted with CeO₂.

The interesting observation is that the DTG curve (Fig. 5) of the pure PANI corresponding to the second-step mass loss of the TG curve shows multi-minima rather than one minimum, which indicates that molecular mass of the pure PANI distributes unevenly. In contrast, the composites corresponding to the second-step mass loss of the TG curve shows one minimum with a small shoulder peak, which indicates that the molecular mass of PANI in the composite distributes more evenly than that of the pure PANI.

Furthermore, the temperature of pure PANI at the minimum of the DTG curve is at 706.5 K, but the minimum temperatures of PANI/CeO₂ composite [70.4/29.6(W/W)] is significantly shifted to a higher temperature by about 77 K. This result suggests again that the composition system is more thermally stable than the pure PANI, which would be explained by the fact that a strong interaction between PANI and CeO₂ restricts thermal motion of the PANI in the composites and enhances thermal stability of the composites.

Conclusions

PANI/CeO₂ composites were prepared by in situ polymerization. IR and XRD results indicated that CeO₂ influenced the structure of PANI through the interaction between PANI chains and CeO₂. This interaction maybe is hydrogen bonding action between the hydroxyl groups on the surface of the CeO₂ and the imine groups in the PANI molecular chains. TG-DTG analysis suggests that the thermal stability of the 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 CeO₂.

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