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Fabrication of Cr_2O_3/Al_2O_3 composite nanofibers by electrospinning

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Abstract PVA(Polyvinyl alcohol)/chromium nitrate/aluminum nitrate composite nanofibers were prepared by using sol–gel processing and electrospinning technique. By high temperature calcinating the above precursor fibers, Cr_2O_3/Al_2O_3 composite nanofibers were successfully obtained. The fibers were characterized by XRD, IR, and SEM, respectively. The results showed that the crystalline phase and the morphology of the fibers depended on the calcination temperatures.

Introduction

Materials with nanometer size particles possess unique chemical and physical characteristic [1, 2]. In particular, nanocomposite materials, composed of nanometric metal and metal oxide particles present a variety of interesting electric, magnetic, and catalytic properties [3–5]. Many efforts have been made to fabricate such materials, including Langmuir–Blodgett film [6], deposition methods [7], synthesis in reversed micelles [8], self-assembled monolayers [9], ball milling technique [10]. Among them, the sol–gel method has also been proposed for the preparation of nanocomposite materials [11, 12]. The process is affected by several parameters which allow a versatile control over the structural, textural, and chemical properties of these materials. Recently, we have found a novel method for making nanofibers of inorganic composite nanomaterials by combining sol-gel processing with electrospinning technique [13, 14]. The small fiber diameters and porous structure of electrospun fibers [15] will result in a high specific surface area that is beneficial in a variety of applications. Proposed uses of these electrospun nanocomposite fibers include electrooptic devices, high sensitive sensors, high active catalyst [16–18], etc. On the other hand, as an important multi-component catalyst, Cr_2O_3/Al_2O_3 composites have been extensively investigated due to its activity in dehydrogenation reactions [19, 20], olefin polymerization, dehydrocyclization reactions, redox reactions [21] and CO-oxidation [22]. In this work, we present a novel method on the preparation of chromium oxide/aluminum oxide composite nanofibers, and want to get a kind of materials that will combine the advantage of nanocomposite metal oxide and electrospun nanofibers mats together. And also hope to obtain a kind of Cr_2O_3/Al_2O_3 composite materials with better catalytic activity and selectivity by virtue of the properties of high surface area and small pore sizes of electrospun nanofibers.

Experimental

Materials

PVA (Polyvinyl alcohol, Mn 80,000) was supplied by Shanxi Chemical Co., Ltd. Analytical-grade chromium nitrate ($Cr(NO_3)_3{\cdot}9H_2O$) and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) were obtained from Aldrich. Distilled water was used as a solvent.

Preparation of $PVA/Cr(NO_3)_3/Al(NO_3)_3$ gels

Firstly, 4.0 mL of chromium nitrate solution (20 wt%) was dropped slowly into 30 mL of PVA solution (7 wt%). After

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stirring for 0.5 h, 4.0 mL of aluminum nitrate solution (20 wt%) was added to the above PVA/$Cr(NO_3)_3$ solution. Then 6.0 mL of ethanol was added under stirring, and the reaction proceeded in water bath at 60 °C for 5h. Thus, a viscous solution of PVA/$Cr(NO_3)_3$/$Al(NO_3)_3$ composites for electrospinning was obtained.

Preparation of nanofibers

The viscous solution of PVA/$Cr(NO_3)_3$/$Al(NO_3)_3$ composites was contained in a plastic capillary. A copper pin connected to a high-voltage generator was placed in the solution, and the solution was kept in the capillary by adjusting the angle between capillary and the fixing bar. A grounded iron drum, covered with aluminium foil, served as the counter electrode. A voltage of 8 kV was applied to the solution and a dense web of fibers was collected on the aluminium foil. The fibers thus formed were dried initially at 80 °C for 12 h under vacuum. At last, the sample was calcined at 700 °C with a rate of 240 °C h^{-1} and remained for 6 h.

Characterization

XRD patterns of the samples were recorded by a Siemens D5005 Diffractometer, scans were made from 10° to 70°(2θ) at the speed of 2° min^{-1}, Ni-filtered CuKα was used. IR spectra were obtained on Magna 560 FT-IR spectrometer with a resolution of 1 cm^{-1}. For SEM investigation, a Hitach-600 was used. BET specific surface areas was determined on an ASAP 2010M at –196 °C of liquid nitrogen.

Results and discussion

X-ray diffraction

XRD spectra of the as-prepared sample and calcined (at 700 °C) fibers are compared in Fig. 1. The broad peak around $2\theta = 20°$ in Fig. 1(a), corresponding to the (101) plane of semi-crystalline of PVA [23], shows that the crystallinity of PVA is largely influenced by the presence of chromium nitrate and aluminum nitrate in the PVA/$Cr(NO_3)_3$/$Al(NO_3)_3$ composite fibers, indicating there may be interactions between PVA and inorganic species. However, after the calcinating at 700 °C in Fig. 1b, the semi-crystalline peak for PVA disappears, and well-defined features is observed due to the crystallization of chromium oxides, which is in agreement with the literature (JCPDS 85-0869). Notably, no significant peaks for aluminium oxides are found due to its amorphous nature before 900 °C [24].

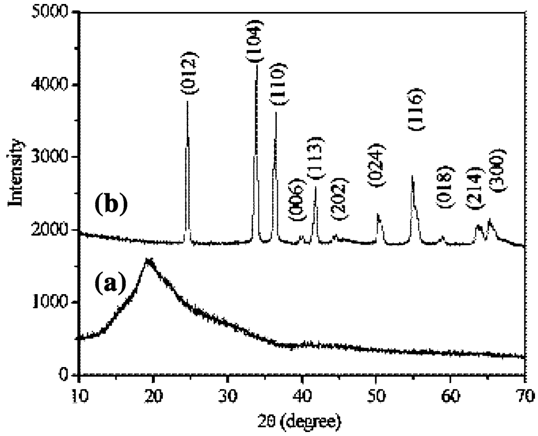

Fig. 1 XRD results for various fibers (**a**) PVA/$Cr(NO_3)_3$/$Al(NO_3)_3$ composite fibers; (**b**) Calcined fibers at 700 °C

FT-IR spectra

Figure 2 gives the FT-IR spectra of various fibers samples. The presence of water in the samples is revealed by the characteristic bands at about 3430 and 1630 cm^{-1} in both Fig. 2a and b. These two bands are respectively identified as O–H stretching and bending mode of vibration. On the other hand, characteristic peaks of PVA disappear in Fig. 2b. They are asymmetric CH_2 stretching or aliphatic C–H stretching at 2933 cm^{-1}, C–H bending or CH_2 scissoring at 1465 cm^{-1}, and C–O stretching at 1094 cm^{-1} [25–27]. Simultaneously, after calcining the sample, new peaks at 635 cm^{-1} and 585 cm^{-1} which assigned to the metal–oxygen vibrations of ν_{Cr-O} and at 400 cm^{-1} which attributed to ν_{Cr-O} and ν_{Al-O} [28, 29] appear in Fig. 2b. Associating with XRD results, one can clearly see that all the organic molecules is removed completely from PVA/$Cr(NO_3)_3$/$Al(NO_3)_3$ composite fibers after calcination at

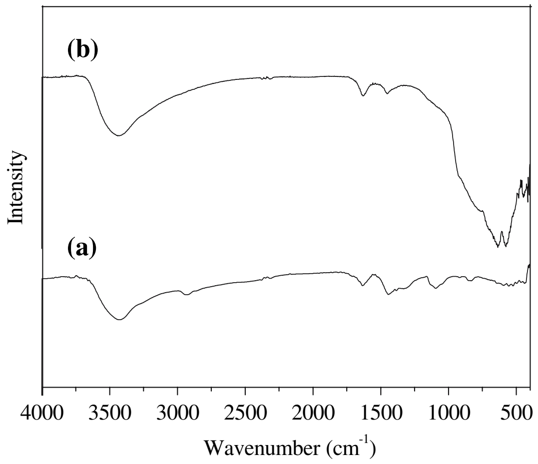

Fig. 2 FT-IR spectra for various fibers: (**a**) PVA/$Cr(NO_3)_3$/$Al(NO_3)_3$ composite fibers; (**b**) Calcined fibers at 700 °C

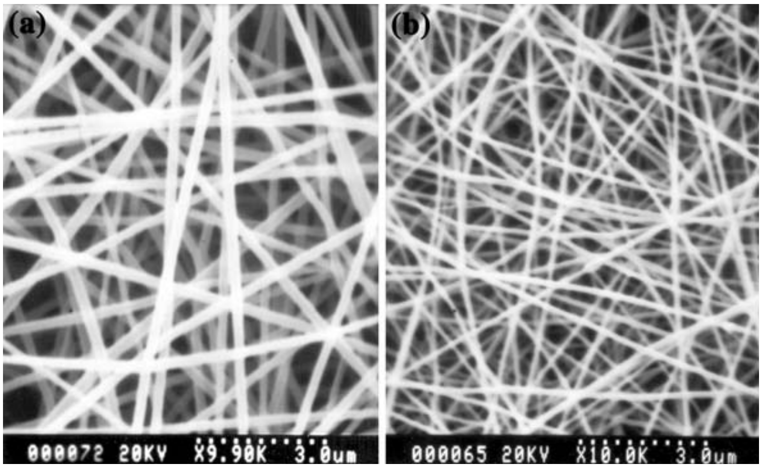

Fig. 3 The morphology of the various fibers: (**a**) PVA/$Cr(NO_3)_3/Al(NO_3)_3$ composite fibers; (**b**) Calcined fibers at 700 °C

700 °C. It indicates that the fibers obtained at this temperature are pure inorganic species, and the formation of Cr_2O_3/Al_2O_3 composite fibers has been confirmed.

Scanning electron microscopy

The SEM photographs of PVA/$Cr(NO_3)_3/Al(NO_3)_3$ composite fibers and the fibers calcined at 700 °C are shown in Fig. 3. It could be seen that the fibers with smooth surface and diameters of 50–150 nm are obtained after calcination. Meanwhile, due to the decomposition of PVA and the removal of NO_3 group of chromium nitrate and aluminum nitrate molecules, the diameters of the fibers calcined at 700 °C (Fig. 3b) become smaller than that of not calcined (Fig. 3a). And, the fibers calcined at 700 °C are still have BET surface area of about 103.25 m^2/g, which indicates that the Cr_2O_3/Al_2O_3 composite fibers might possess high catalytic activity due to its high surface area.

Conclusion

For the first time, composite Cr_2O_3/Al_2O_3 nanofibers, with the diameter of 50–100 nm, were fabricated by calcining the electrospun nanofibers of PVA/$Cr(NO_3)_3/Al(NO_3)_3$ composites. This facile approach might promise us some possible applications of one-dimensional Cr_2O_3/Al_2O_3 composite. By modifying the parameters of sol–gel method and electrospinning process, one could also expect to fabricate nanofibers of composite materials with smaller diameter.

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