Fabrication and Sensing Behavior of Cr_2O_3 Nanofibers via In situ Gelation and Electrospinning

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In this paper, we developed an in situ gelation method to simplify the electrospinning technique. Chromium hydroxide/polyvinyl alcohol (PVA) hybrid nanofibers were prepared by electrospinning technique and in situ gelation. Ultrathin fibers of chromium oxide with 150–200-nm diameters were obtained by high-temperature calcination of the hybrid fibers. Structural, morphological, and crystalline phase features of electrospun Cr_2O_3 nanofibers were studied by SEM, XRD, and DTA-TGA. Ethanol-sensing behavior of the nanofibers was also investigated.

One-dimensional (1D) nanostructures, including nanofibers, nanotubes, nanorods, nanobelts, etc., are highlighted for their unique properties and potential value of application. Plenty of methods were developed to prepare 1D materials. Electrospinning is a new technique that can be used as a simple and versatile method for preparing ultrathin structure such as polymer fibers, ceramic nanofibers, or organic/inorganic composite. Materials prepared by electrospinning attract much attention for the applications in many fields such as catalysts, sensors, biomedical applications, filtration, and templating.[1] In recent years, many researches focused on the preparation of pretty long inorganic nanofibers[2] and organic/inorganic hybrid nanofibers[3] with diameter of tens to hundreds nanometer range via electrospinning.

The classic route to prepare inorganic nanofibers contents three main steps: a) preparation of a solution containing polymer and metal hydroxide sol, b) collection of organic/inorganic composite nanofibers, c) calcination of the composite nanofibers.

Preparation of metal hydroxide gel/polymer hybrid is a key step of preparing inorganic nanofibers. The formation of this hybrid will keep the shape of the nanofibers when calcinated. By the traditional method, the preparation of this hybrid needs precursors containing metal hydroxide sol which usually needs organometallic compound and more than 12 h to prepare.[4] In this work, we have developed an in situ gelation method which merely needs ion/PVA solution as precursor. The new method needs four steps: a) preparation of a solution containing polymer and metal ion, b) collection of composite nanofibers, c) treating the nanofibers with alkaline gas to form gel/polymer hybrid fibers, d) calcination of the hybrid nanofibers. In fact this technique is a simple and efficient way to prepare inorganic nanofibers.

Chromium oxides have already been used as commercial catalyst in the polymerization of ethylene and in the dehydrogenation of light paraffin.[5] As a semiconductor metal oxide, chromium oxide is a good sensor to sense hydrogen in air and oxygen in hydrogen.[6] Chromium oxide nanofibers may show more and better properties because of the huge specific surface area and high length/diameter ratio. In this work, we describe the preparation of Cr_2O_3 nanofibers via electrospinning and their characterization. The ethanol sensitivity of the nanofibers is investigated, and a comparison between nanostructure and ordinary powder will be given.

The PVA solution (9 wt %) was first prepared by adding PVA powder in distilled water and heating at 80 °C with stirring for 2 h, then cooling to room temperature. The spinning solution can be obtained by dissolving 1 g of $CrCl_3 \cdot 6H_2O$ in 5 mL of PVA solution. The solution was placed in a plastic hypodermic syringe whose pinhead connected to a high-voltage generator. A sheet copper, covered with a filter paper, served as the counter electrode. Silicon wafer was placed on the paper as the receiver of nanofibers. The distance between the pinhead and the receiver is about 10 cm. A voltage of 20 kV was applied to the solution, and a light green fiber film was collected on the silicon wafer. We treated the wafer with composite fibers with NH_3 for half an hour; the color of the film turned into sage green, and the fibers was no longer sticky. The wafer with nanofibers were preoxided 2 h at 200 °C in air to avoid the PVA melting. After this it was calcined at 700 °C in air for 6 h.

Figure 1 shows thermal behavior of PVA/$Cr(OH)_3$ hybrid fibers. As observed in the differential thermal analysis (DTA) curve, a strong endothermic peak could be found at ca. 250 °C, which corresponded to the loss of hydroxy group. The exothermic peak around 300 and 440 °C in the DTA curve may indicate the decomposition on the side and main chains of PVA. Because of the formation of α-Cr_2O_3 crystals, which was called "glow phenomenon,"[7] there was a strong sharp peak in DTA curve at 403 °C and a nearly vertical weight lose step in TGA curve at 390 °C. For the TGA curve, most of the organic belonged to PVA, and the combined water of $Cr(OH)_3$ was removed at a temperature below 500 °C. There was no more weight loss above 500 °C, indicating the formation of pure chromium oxide.

The XRD patterns for the Cr_2O_3 nanofibers in Figure 2 show that the crystalline phases present in the fiber after calcination treatment. All the peaks can be well indexed to the crystallographic phase of hexagonal Cr_2O_3 (JCPDS84-1616). No peaks from any other phase or impurities were found, which indicated

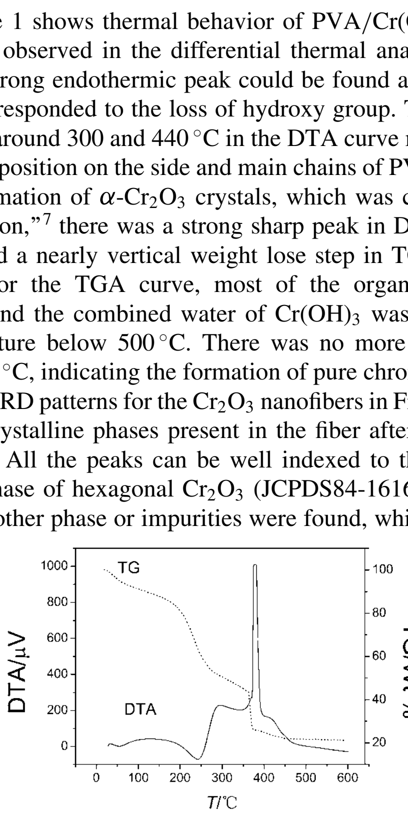

Figure 1. TGA-DTA curves of the PVA/$Cr(OH)_3$ hybrid fibers.

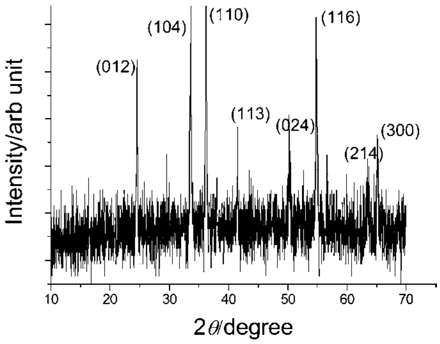

Figure 2. XRD pattern of Cr_2O_3 nanofibers.

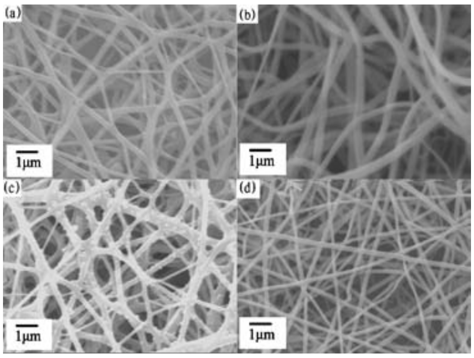

Figure 3. SEM images of: (a) $CrCl_3$/PVA composite nanofibers, (b) $Cr(OH)_3$/PVA hybrid nanofibers, (c) $Cr(OH)_3$/PVA hybrid nanofibers placed in air for two weeks, (d) fibers calcinated at 700 °C for 6 h.

the high purity of the Cr_2O_3 nanofibers.

Figure 3 shows morphologies of the various fiber samples revealed by scanning electron microscopy (SEM). It could be seen that the surface of both as-prepared composite fibers and NH_3-treated fibers were smooth (Figures 3a and 3b). And after placed in air for two weeks, the surface of NH_3-treated fibers is no longer smooth. That may indicate that the small $Cr(OH)_3$ particle in the gel grows during the two weeks (Figure 3c). After calcination of NH_3-treated fibers (Figure 3b) at 700 °C (Figure 3d), the diameters of the fibers became smaller. The calcined fibers have a smooth surface and uniform diameter of 150–200 nm.

As a semiconductor material, Cr_2O_3 has sensitivity to some gas. In this work, we investigated the property of the Cr_2O_3 nanofibers and ordinary powder as ethanol sensor by HW-C30A system (Henan Hanwei Electronics Co., Ltd.). The sensors were fabricated using thin film of the materials simply. By monitoring the resistance of the film, the response of the sensor in air can be measured. Figure 4 plots the change in sensor resistance as a function of time when the sensor was working at 400 °C. Seven cycles were successively recorded, corresponding to seven different ethanol concentrations ranging from 10 to 1000 ppm. The resistance of nanofibers underwent a drastic rise on the injection of ethanol and drops to its initial value immediately after ethanol was released. Both the sensors showed good response, but the ordinary powder showed a much milder one. Reaction mechanism[8] of p-type semiconductor to detected gas may explain the sensing property of Cr_2O_3. When in contact with the gas to be detected, the density of negatively charged oxygen absorbed on the surface would change, and the resistance of the semiconductor was changed too. In this test, the sensor of nanofibers possessed more advantages. Surface absorbed charged oxide is very important so huge specific surface area of the nanofibers is believed necessary to high sensitivity. Here, the resistance of the nanofibers is low since the 1D structure can increase the conductivity of the materials, and the structure may be also helpful to its sensitivity.[9]

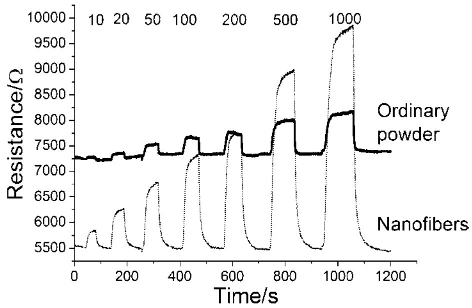

Figure 4. Typical response curves of nanofibers and ordinary powder on cycling between increasing concentration (10–1000 ppm) of ethanol and ambient air.

In conclusion, we have developed in situ gelation method to simplify the route to fabricate oxide nanofibers via electrospinning technique. This route might be more efficient and inexpensive than the classic route. By this route, Cr_2O_3 nanofibers, with diameters in the range of 150–200 nm, were prepared after calcination of $Cr(OH)_3$ gel/PVA hybrid. The gas-sensing measurement shows that Cr_2O_3 nanofibers have benefits to the sensitivity of ethanol vapor. It also indicates that we can develop many useful devices by electrospinning technique.

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