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Review paper

Electrospinning preparation and characterization of alumina nanofibers with high aspect ratio

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Abstract

Alumina nanofibers were successfully prepared via an electrospinning technique combined with a sol–gel method. The electrospinning solution was prepared by dissolving aluminum isopropoxide (AIP) in distilled water and then mixing with a polyvinyl alcohol (PVA) aqueous solution. The as-spun fibers were calcined at different temperatures and characterized by TG–DTA, XRD, SEM–EDS, TEM–SAED, and BET analysis. Results showed that the average fiber diameter decreases with increasing calcination temperature. The as-spun nanofibers were amorphous. After calcination at 1000 °C, the nanofibers formed were composed of α-Al_2O_3 and γ-Al_2O_3, showing an average diameter of 30–90 nm and an aspect ratio of greater than 1000. The pore size of the obtained fibers was approximately 5 nm, which implies that these fibers are mesoporous materials.

Keywords: A. Calcination; Alumina; Nanofibers; Electrospinning; Sol–gel

Contents

1. Introduction

Alumina (Al_2O_3) is an excellent ceramic oxide with a very wide range of applications, including adsorbents, catalysts, microelectronics, chemicals, aerospace industry, and other high-technology fields [1–4]. One-dimensional (1D) nanostructured Al_2O_3 materials, such as nanofibers and nanorods, have attracted significant interest over the past decade because of their well-defined size and large surface area to volume ratio [5–11].

Electrospinning is a valuable method used exclusively for the direct and continuous preparation of nanometer polymer

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fibers [12–22].Electrospinning is a process by which a polymer solution or melt can be spun into fine-diameter fibers using external electrical forces. Several polymeric nanofibers with diameters of several micrometers to tens of nanometers have been produced by electrospinning. The combined use of electrospinning with a sol–gel process to produce fibers has recently attracted the attention of the scientific community. The fibers prepared through this method are of small and uniform diameter and demonstrate excellent performance. In this electrospinning method, a sol is first prepared via the sol–gel method, after which a spinning solution of a certain viscosity is prepared by mixing a polymer and sol. Raw fibers are prepared by electrospinning of the spinning solution and subsequent decomposition to obtain oxide fibers [23–26]. A series of nanofibers, such as those of TiO_2, CeO_2, SnO_2, ZrO_2 and SiO_2 [27–31] have been prepared using this method. Most of these fibers are polycrystalline in nature.

To the best of our knowledge, the preparation alumina nanofibers with average diameters of less than 100 nm using the electrospinning technique has rarely been reported. In most of the previous research on the sol–gel method [23–26,32,33], the electrospinning sol used ethanol or ethanol/water as a solvent, and the average diameter of the resultant alumina nanofibers exceeded 100 nm.

In this study, we present a simple and convenient method to prepare alumina nanofibers with diameters of 30–90 nm. The electrospinning solution was prepared by dissolving aluminum isopropoxide (AIP) in distilled water and then mixed with a polyvinyl alcohol (PVA) aqueous solution. The nanofibers obtained were characterized by TG–DTA, XRD, SEM–EDS, and TEM–SAED to study their microstructural and compositional evolution. This work provides a simple and low-cost route to synthesizing mesoporous alumina nanofibers with a wide range of potential applications in various industries.

2. Experimental procedure

2.1. Preparation of alumina sol and nanofibers

Aluminum isopropoxide (AIP) with a reagent grade of 99% from Tian Jin Jin Ke chemical industry was used as the source of alumina precursor. Polyvinyl alcohol (PVA-124) purchased from Xi Long chemical reagent company was used as the polymer precursor. Nitric acid (HNO3) and ethyl acetoacetate were obtained from Beijing chemical industry company.

For the electrospinning experiments, a set amount aluminum isopropoxide was dissolved in distilled water. Some nitric acid and ethyl acetoacetate were added to the aluminum isopropoxide solution. The solution was magnetically stirred at 85 °C for 16 h to produce AlOOH sol. Similarly, the PVA solution was made by dissolving PVA in hot water (80 °C). The suitable electrospinning solution was prepared by mixing AlOOH sol and PVA solution with a magnetic stirrer, which was electrospun at ambient temperature with optimized voltage of 20 kV. The as-spun fibers were calcined at 500, 700 and 1000 °C with a rate of 3 °C/min for 5 h in air.

2.2. Characterization

Thermal analysis was performed under air and at a heating rate of 5 °C min^{-1} (Netzsch STA 409, Germany). Phase identification was carried out by X-ray diffraction (XRD) (PANalytical X'Pert PRO diffractometer, PANalytical Corporation, the Netherlands) with CuKα radiation. Scanning electron microscope (SEM, XL30, Philips-FEI, Eindhoven, the Netherlands) and transmission electron microscope (TEM, JEM-2100 CX, Jeol, Japan) were used for determination of fiber diameter and examination of microstructure. The surface area was determined by the Brunauer–Emmett–Teller (BET) method, and the pore volume and pore size distribution were determined by the non-local density functional theory (DFT) method.

3. Results and discussion

3.1. The thermal behavior of the as-spun nanofibers

Transparent AlOOH sol could be obtained by controlling the ratio of aluminum isopropoxide, water, and nitric acid, as well as the hydrolysis temperature. The prepared AlOOH sol and its Tyndall phenomenon are shown in Fig. 1.

SEM images of nanofibers with different PVA contents are illustrated in Fig. 2. Only submicron-scale particles were produced by the electrospinning solution without PVA (Fig. 2a) because of the low viscosity of the solution. When the PVA contents of the solution were 1% and 2%, the as-spun nanofibers obtained were bead-like (Fig. 2b and c). When the PVA content was increased to 3%, the as-spun nanofibers were relatively uniform (Fig. 2d); nanofibers with 4% PVA showed even better characteristics (Fig. 2e) because the size distribution of the as-spun nanofibers was uniform. As PVA content increased, the diameters of the as-spun fibers also increased, as shown in Fig. 2f.

Based on the results described above, the solution with 4% PVA content was prepared for electrospinning. The thermal behavior of the as-spun nanofibers at temperatures of up to 1000 °C was studied by TGA–DTA in air. The TGA–DTA curves of the as-spun nanofibers are presented in Fig. 3. The figure shows three major weight loss events in the fibers. The first weight loss of 7 wt% occurred between 30 and 200 °C because of evaporation of residual moisture and ethanol molecules in the fibers. The second weight loss (55%) began at 200 °C and was caused by thermal decomposition. At temperatures exceeding 560 °C, another weight loss of 1 wt % occurred; at this point, the PVA was completely decomposed. The associated DTA curve shows a broad exothermic peak and an endothermic peak. The exothermic peak in the range of 200–560 °C is associated with the significant weight loss and decomposition of PVA. The endothermic peak occurring from 560 °C to 1000 °C can be attributed to the phase transition, melting, and recrystallization of alumina.

3.2. Morphology and phase evolution

According to the TGA–DTA results, the as-spun fibers were calcined at 500, 700, and 1000 °C. The XRD patterns of the