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Effects of precursor concentration on crystalline morphologies and particle sizes of electrospun WO_3 nanofibers

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Abstract

Tungsten oxide (WO_3) nanofibers with different crystalline morphologies and various particle sizes were fabricated using an electrospinning technique. The nanofibers were prepared from mixtures of polyvinyl alcohol (PVA) and ammonium metatungstate hydrate (AMH) of various concentrations ranging from 4.2%w/v to 50.0%w/v. After calcination at 500 °C for 2 h, the nanofibers were observed to have a monoclinic crystal structure with diameters ranging from 30 to 250 nm. AMH concentration had a large influence on the resulting nanofiber morphology. Very low AMH concentration of 4.2%w/v led to the formation of WO_3 nanofibers having a very large area of monocrystalline structure. Higher AMH concentrations result in polycrystalline WO_3 nanofibers with joined nanoparticles along the fiber axis. The average particle size within the nanofibers increased from 29 to 66 nm as the AMH concentration increased from 8.3%w/v to 50%w/v. At these precursor concentration levels, primary particles were formed before PVA was completely burnt off, resulting in agglomeration of primary particles along the nanofiber axis.

Keywords: Tungsten oxide; Electrospinning; Nanofibers; Precursor concentration; Crystalline morphology

1. Introduction

Metal-oxide semiconductors such as SnO_2, TiO_2, ZnO, In_2O_3, and WO_3 are an important class of materials because of their various potential technical applications [1]. Among these metal-oxide semiconductors, WO_3 has received much attention because it offers several useful properties including sensing [2-7], electrochromism [8–10] and enhanced catalytic behavior [11–13]. Recently, there has been a great interest in the synthesis of WO_3 into one-dimensional (1D) structures such as nanorods [2,5,6,12,13,14–17], nanowires [3,4,7,17–19], and nanotubes [20,21]. This is because 1D structures offer high surface areas and unique electron transport properties [22]. Most recently, 1D WO_3-based nanofibers fabricated by electrospinning gained interest due to their large number of potential applications [23–27].

Electrospinning is a versatile technique that can be used to synthesize many different materials into fibrous forms with diameters in the range of 20–2000 nm [23,24]. This technique is cost-effective and can be used for large-scale production [23–25]. Recent advances in the field have led to the production of new nanofiber materials, some with even more complex structures [28–30]. For instance, new research reported the use of electrospinning to produce an active drug crystal/polymer composite in nanofiber form [29]. Nanoparticles with anisotropic morphology have also been produced by the electrospinning method [30]. Use of electrospinning to fabricate polymer scaffolds for the dispersion of new functional materials may be useful in future technical applications. However, new models and more understanding of particle formation within the nanofibers are still needed.

In this work, we studied the formation of WO_3 particles within electrospun nanofibers. Fabrication by electrospinning consists of mixing inorganic precursors with a polymer used to control the mixture's viscosity. Viscous liquid is then pulled under an electric field onto a metal collector. The resulting nanofibers are then calcined at an elevated temperature to decompose the polymer while allowing the inorganic precursors to oxidize and form WO_3 nanoparticles aligned along the fiber axis. Efforts have been made to control the diameter of the nanofibers by adjusting the viscosity of the solution and

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by changing the parameters of the electrospinning setup. However, reports on the synthesis parameters affecting crystalline morphology and the size of particles within the fibers are limited. The physicochemical properties of WO_3 are dissimilar for different polymorphs. Thus, nanoscale control of sizes and crystalline morphologies is very important. In this paper, we discuss the effect of precursor concentration on morphologies and particle sizes of WO_3 nanofibers. Fabrication steps that allow the production of WO_3 nanofibers with a very large area of monocrystalline structure using the electrospinning technique are reported for the first time. We also propose a model to explain the formation of nanofibers with different crystalline morphologies and particle sizes that occur during the calcination process.

2. Experimental

Tungsten oxide precursor solutions were prepared by mixing ammonium metatungstate hydrate (AMH) in de-ionized water (DI) at concentrations of 4.2%w/v, 8.3%w/v, 16.7%w/v, 33.3%w/v and 50.0%w/v. The solutions were stirred at room temperature for 15 min. A polymeric solution was prepared by mixing polyvinyl alcohol (PVA) in DI water and stirring for 40 min at 95 °C. The polymer liquid was then allowed to cool to room temperature. The resulting polymer solution was used to control the viscosity of the solution. Its concentration was fixed at 7%w/v in all experiments in the current study. Both tungsten oxide and polymeric solution were then mixed and stirred vigorously for another 24 h at room temperature. The electrospinning conditions were as followings: a high-voltage DC power supply was set to 19.5 kV, feed rate was 0.1 ml/h, and distance between the needle and the metal collector was 15 cm. Finally, calcination was carried out at 500 °C for 2 h to eliminate polymer from the resulting fibers. In this step, temperature ramp up/down rates were set to 1 °C/min. These slow heating and cooling rates are crucial to prevent fiber agglomeration and loss of as-spun fibrous structures.

Thermo-gravitational analysis (SHIMADZU 50/50H TGA) was used to find an optimized calcination temperature of the nanofibers. X-ray diffraction (PHILIPS PW1830 XRD) was used to analyze the crystal structure of WO_3 nanofibers. Average diameters and shapes of the WO_3 nanofibers were characterized using scanning electron microscopy (Hitachi S-3000N SEM). Transmission electron microscopy (FEI Tecnai G2 20 TEM) operated at 200 keV was used to characterize the structures and the particle sizes of nanoparticles within the resulting fibers. The average particle sizes of the WO_3 nanofibers were measured in 300 randomly selected locations of each sample. A high-resolution TEM (HRTEM) technique was employed to investigate, in detail, the atomic structure of the samples. The HRTEM condition was achieved by carefully correcting the astigmatism of the objective lens of the microscope. Images were taken near a Gaussian defocus condition to improve the contrast. Selected area electron diffraction (SAED) was performed to characterize the crystalline morphologies of the samples.

3. Results and discussion

Fig. 1 shows a typical TGA curve of the AMH/PVA composite nanofibers produced using the electrospinning technique. In region I indicated by a red arrow, the 4.1% weight loss was due to evaporation of moisture and trapped solvent at 25–85 °C. In region II, the 22.3% weight loss was due to the degradation of PVA at 154–474 °C. In region III, the 10.3% weight loss was due to decomposition of the PVA polymeric chain backbone at 474–500 °C. Finally, in region IV, there was no significant change in sample weight above 500 °C since all PVA was fully decomposed. From this TGA result, it can be concluded that a temperature of 500 °C is enough to fully decompose PVA within the nanofibers. Higher calcination temperature can be used. However, treating the precursor at too high a temperature would result in grain growth and may affect the overall structure of the nanofibers. Since the goal of the current study was to elucidate the effects of precursor concentration on the resulting particle sizes and morphologies, calcinations conditions of 500 °C for 2 h were used. This was done to ensure complete removal of PVA while minimizing grain growth during the calcination process.

An image of the resulting nanofibers produced using different AMH concentrations is given in Fig. 2. The nanofibers appear to be continuous. Their diameters range from 30 to 250 nm. It was observed that fabrication using lower precursor concentrations generally leads to nanofibers with smaller diameters. This results from lesser amounts of starting material available to form the final WO_3 product. It is notable that an AMH concentration of 4.2%w/v was the lowest concentration in our experiments that allowed the formation of continuous fibers.

The crystal structure of WO_3 nanofibers was characterized using an XRD technique. The results are shown in Fig. 3. The diffraction spectra are well in agreement with the JCPDS database no. 83-0951 [31], indicating a monoclinic crystal structure.

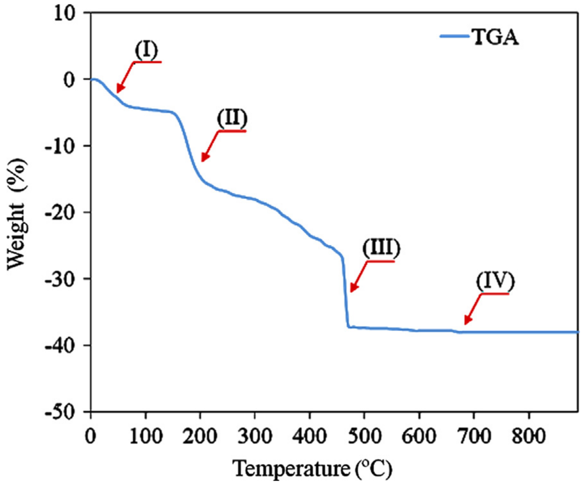

Fig. 1. Typical TGA curve of AMH/PVA composite nanofibers. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)