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Titania nanofibers prepared by electrospinning

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ABSTRACT

TiO_2 nanofibers with a diameter of 54–78 nm have been successfully prepared by electrospinning method using a solution that contained poly(vinyl pyrrolidone) (PVP) and Ti(IV)-isopropoxide. The effect of viscosity and applied electric field on the morphology of the electrospun titania fibers was investigated. It has been observed that the increase in electric field causes bead formation and discontinuity in nanofiber morphology.

1. Introduction

Titanium dioxide is a key functional material that has been extensively used in applications related to environmental cleaning and protection, photocatalysis, gas sensing and fabrication of solar cells and batteries [1–3]. Various preparation methods for TiO_2 whiskers, nanorods and nanotubes, including sol–gel, dip-coating, and electrochemical methods have been reported [4]. Novel metal oxide nanofibers and nanotubes, such as titanium oxide, alumina borate, silica, cobalt oxide, nickel oxide, tin oxide, zirconium oxide, copper oxide, niobium oxide, palladium oxide, vanadium oxide and zinc oxide have been successfully prepared by electrospinning process [5–15]. Based on these studies it is clear that characteristics such as fiber diameter, fiber morphology and the density of beads are strongly depending on the solution concentration, viscosity, surface tension and conductivity and process variables, such as applied voltage, needle diameter, flow rate and needle-to-collector distance.

In the present work, formation of titanium dioxide nanofibers using the electrospinning technique and the effect viscosity and of electric field on nanofiber morphology was investigated.

2. Experimental

1.5 mL of Ti(IV)-isopropoxide, and 3 mL of acetic acid were added to 10 mL of ethanol containing 0.45 g of polyvinyl pyrrolidone (PVP, Aldrich, Mw 1,300,000) were used as the starting chemicals. The mixture was vigorously stirred at room temperature to get a homogeneous polymer solution. The solution was loaded into a plastic syringe equipped with a 22-gauge stainless steel needle. The needle was connected to a high-voltage supply (Gamma High Voltage ES30) and the solution was fed at a constant rate (0.3 mL/h) using a syringe pump (Top Syringe Pump Top-5300). A piece of flat aluminum foil was placed below the tip of the needle to collect the nanofibers by applying an electric field of 1, 1.25 and 2 kV/cm. The as-spun nanofibers were heat treated at 600 °C for 3 h in order to remove PVP and crystallize TiO_2.

The prepared sol used in the electrospinning was dried at 100 °C for 1 h and the obtained powder subjected to thermogravimetric differential thermal analysis (DTA/TG) (Shimadzu DTG-60H). The viscosity of the prepared sol was measured at 30 °C by using a Brookfield DV-E model viscometer. The X-ray diffraction (XRD) measurements were performed for crystal phase identification (Rigaku D/Max-2200/PC) with CuKα radiation. The morphology and average fiber diameter of nanofibers was characterized by scanning electron microscope (JSM-6060 JEOL).

3. Results and discussion

DTA/TG analysis of the prepared TiO_2/PVP sol is shown in Fig. 1. The DTA curve depicted an exothermic peak at 80 °C, which indicates the loss of solvent such as water,

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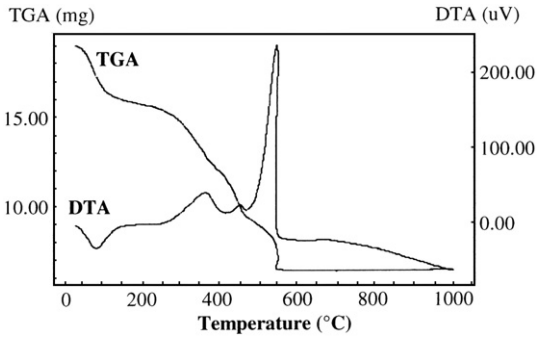

Fig. 1. DTA/TG analyze of the prepared sol used to prepare TiO_2 nanofibers.

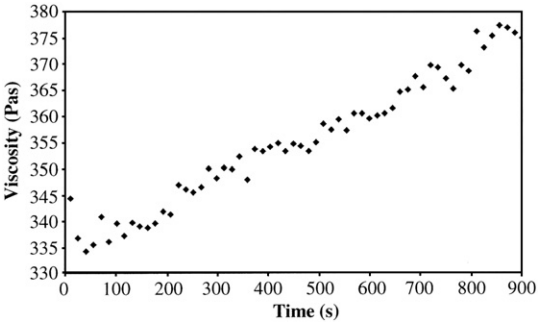

Fig. 2. Viscosity of the prepared sol used to prepare TiO_2 nanofibers.

ethanol and carbon dioxide. There are two endothermic peaks at 360 °C and 550 °C, which indicates the degradation of PVP and the formation of crystalline TiO_2, respectively. The weight loss was in the range of more than 65%. Crystallization (heat treatment) temperature was chosen as 600 °C which corresponds to the end of the exothermic reaction.

To produce a uniform nanofiber, surface tension and surface charge act in competition while viscosity plays a major role as well. As seen from Fig. 2, the viscosity of the prepared sol increases with time (time-dependent) and indicates that the prepared sol is not stable. Also, the absence of a rapid increase in viscosity shows that the phase separation occurred at relative short period of reaction time. It has been reported that, as the viscosity of a solution is increased, bead size increases, and the shape of the beads becomes more spindle shaped than spherical [16]. However, during the electrospinning process, no change in the morphology has been observed due to the increase in viscosity. This contradiction may be due to the humidity in air and hydrolysis reactions occurring in the solution during the viscosity measurements.

Fig. 3 gives the XRD patterns of nanofibers heat treated at 600 °C. The crystalline peaks indicate that the crystal structure of TiO_2 is in the form of mixed anatase and rutile.

The magnitude of the electric field is a key factor that determined the morphology and diameter of the electrospun fibers [5]. Fig. 4 shows the SEM micrographs of heat

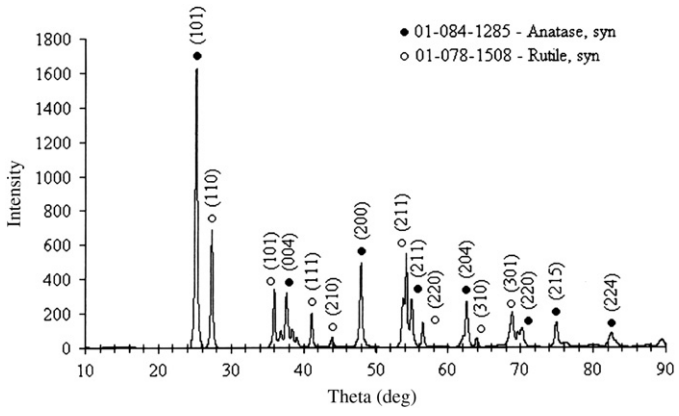

Fig. 3. XRD result of the prepared TiO_2 nanofibers.

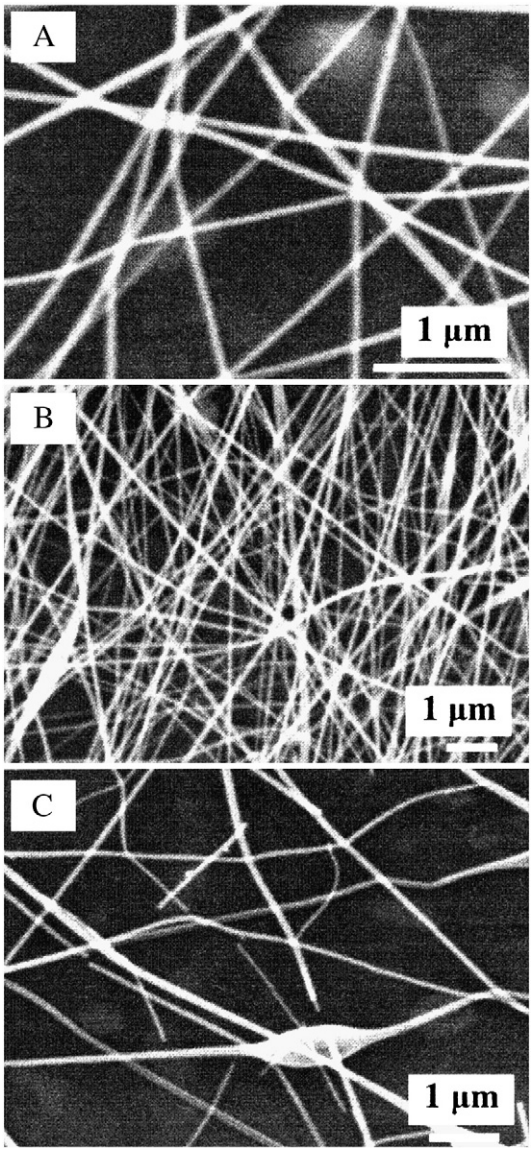

Fig. 4. SEM images of TiO_2 nanofibers prepared at A) 1, B) 1.25 and C) 2 kV/cm of electric field.

treated TiO_2 nanofibers prepared at different electric fields. The diameters of these fibers were quantitatively evaluated using their high-magnification SEM images. Each individual nanofiber was uniform in cross section and the average diameter of samples prepared at 1, 1.25 and 2 kV/cm of electric field was 78, 63 and 54 nm, respectively. Bead formation is a common problem in nanofibers prepared by electrospinning. From Fig. 4, it can be clearly seen that sample A demonstrate a bead-free morphology, however the density of beads increased as the electric field was increased. Also, as seen from Fig. 4C, increasing the electric field up to 2 kV/cm causes a discontinuity. Li and Xia, reported that the bead formation is related with the stability of the liquid jet and increasing voltage would change the shape of the drop and a stable, conical shape could not be achieved [5]. As a result, an increase in the electric field decreases the nanofiber size but increases the density of beads. However, increasing the electric field over a certain limit causes a discontinuity.

4. Conclusions

TiO_2 nanofibers with a diameter of 54–78 nm have been successfully prepared by electrospinning. It has been found that viscosity of the prepared sol does not affect the fiber morphology. TiO_2 was in the form of mixed anatase and rutile after a heat treatment at 600 °C for 3 h. It has been observed that increasing the electric field causes bead formation and discontinuity in nanofiber morphology.

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