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Effect of collector grounding on directionality of electrospun titania fibers

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Abstract

TiO_2 nanofibers were prepared by using electrospun TiO_2/polyvinylpyrrolidone fibers by drying for 5 h in air and subsequent annealing for 3 h at 500 °C. Uniform and smooth fibers with diameters of 120 ± 10 nm were observed at a PVP concentration of 0.09 g/ml, a $Ti(OCH(CH_3)_2)_4$ concentration of 0.14 g/ml, a flow rate of 0.5 ml/h, and an electric field of 1 kV/cm, respectively. TiO_2/PVP nanofibers were also electrospun by varying the collector grounding design to improve the axial alignment of fibers. The collector is composed of two pieces of conductive substrates separated by a gap of 1.5 mm. In addition, the collector consisting of two sets of substrates placed by 90° are prepared for a grid structure of the fibers. Both collectors show that the charged nanofibers are stretched to span across the gap between the electrodes.

Keywords: Titania; Sol-gel processes; Fibres; Electrospinning

1. Introduction

One-dimensional nanostructures have been investigated extensively for their potential applications such as electronics, optoelectronics, mechanics, catalysis, and biological and environmental systems, because of their unique properties.[1–3] Oxide-based titania (TiO_2) photocatalysts are widely used as air, water treatment, and deodorizer due to the large specific surface area, strong oxidizing power, high photocatalytic activity, self-cleaning function, and bactericidal activity.[4,5] It is noted that titania whiskers, nanorods, and nanotubes have been synthesized using sol–gel and electrochemical methods with channels in anodic alumina membranes.[6–8] This process is somewhat time-consuming in obtaining the oxide-based nanostructures. It is composed of three steps, fabrication of templates, coating of the surfaces of templates with titania, and removal of the templates. To curtail the multiple steps, an electrospinning technique was employed to synthesize fibular mesostructures due to the simplicity.[9,10]

Electrospinning is a method of producing fibers by accelerating a jet of charged polymer solution in an electric field.[9–12] A high-voltage power supply generates an electric field between a syringe with a capillary tip and a grounded collector. Electrostatic charging of the fluid at the tip of the nozzle results in formation of the well known Taylor cone, from the apex of which a single fluid jet is ejected.[11,12] As the jet accelerates and thins in the electric field, radial charge repulsion results in splitting of the primary jet into multiple filaments. These fibers are collected on the surface of a collector as highly impermeable, nonwoven mats that are characterized by high surface area and relatively small pore sizes.[11,12]

Recently, the spatial orientation of electrospun fibers has been attempted to obtain well aligned and highly ordered for use with microelectronic and photonic devices.[13] Although there are several attempts to achieve the fiber alignment mechanically by varying the collector geometries such as rotating drum[14] and wheel-like bobbin, it may be not feasible to obtain highly ordered fibers over large area. In the present study, TiO_2/polyvinylpyrrolidone (PVP) nanofibers were electrospun by varying the collector grounding design to improve the axial alignment of fibers. The collector is composed of two pieces of conductive substrates separated by a gap of 1.5 mm. In addition, the collector consisting of two sets of substrates placed by 90° are prepared for biaxial alignment of fibers.

2. Experimental procedure

The precursor solution was prepared from titanium tetraisopropoxide ($Ti(OCH(CH_3)_2)_4$, 98%, Aldrichi, USA) in ethanol

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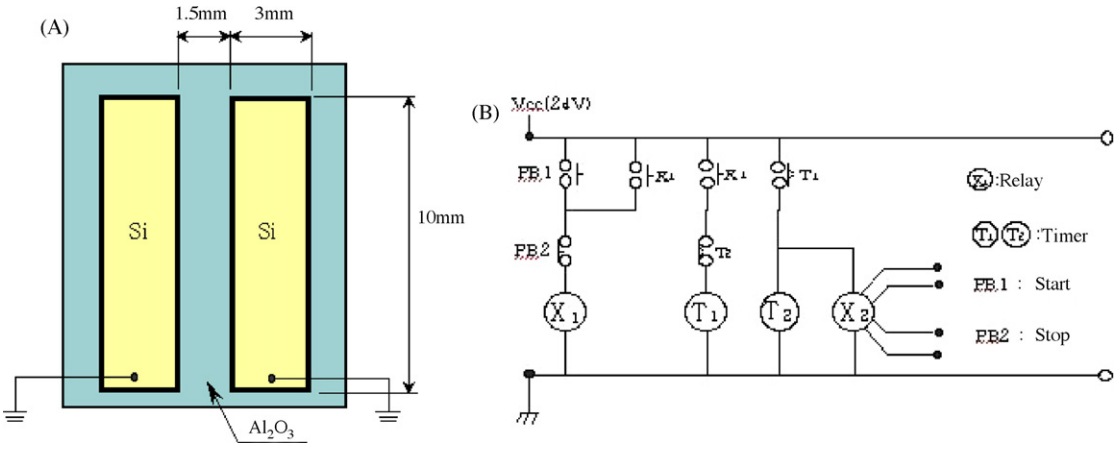

Fig. 1. Schematic diagram of the setup for (a) uniaxial alignment of the fibers and (b) of an electrical circuit for biaxial alignment of the fibers.

by stirring. PVP (M_w = 1,300,000, Aldrichi, USA) dissolved in ethanol and acetic acid was added to the TiO_2 precursor solution by weight. The solutions were mixed and stirred for 1 h at room temperature. The electrospinning apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22 gage metal needle, a grounded collector, and a high-voltage supply (ES30P-5W, Gamma High Voltage Research Inc., USA) equipped with current and voltage digital meters. The solution was placed in a 5 ml BD luer-lok syringe attached to the syringe pump and fed into the metal needle at a flow rate of 0.1–1.2 ml/h. A piece of flat aluminum foil was placed 5–15 cm below the tip of the needle to collect the nanofibers. The as-spun nanofibers were dried in air for 5 h to allow the hydrolysis of $Ti(OCH(CH_3)_2)_4$. Subsequently, annealing for 3 h at 500 °C in air with a heating rate of 1 °C/min was performed to remove the PVP and achieve the crystallization of titania.

The nanofibers were characterized by measuring the viscosity, the surface tension, and the fiber morphology. The kinematic viscosity, the surface tension and the density of the precursor solution were determined by a Cannon-Fenske viscometer, a goniometer (Surface Tech Co., Korea) and a pycnometer, respectively. The dynamic viscosity was calculated from kinematic viscosity and density data. The diameter and the morphology of the nanofibers were evaluated using a scanning electron microscope (SEM, Hitachi S-3000H, Japan). All specimens were coated with Au/Pd to ensure higher conductivity. For SEM observation, the titania nanofibers were prepared by placing silicon wafers on the aluminum foil during electrospinning. The crystalline phase of the nanofibers was analyzed by using X-ray diffraction (XRD).

The optimized TiO_2/PVP nanofibers were electrospun by varying the collector grounding design to improve the axial alignment of fibers, as shown in Fig. 1. The collector is composed of two pieces of Si substrates separated by a gap of 1.5 mm. In addition, the collector consisting of two sets of copper substrates (15 mm) placed by 90° are prepared for biaxial alignment of fibers. The collection times were 3 s at each axis, which was controlled by the timer as depicted in Fig. 1(b).

3. Results and discussion

The parametric dependency studies for the fabrication of titania nanofibers, such as PVP concentration, $Ti(OCH(CH_3)_2)_4$ concentration, flow rate and electric field, are reported elsewhere.[10] It was noted that the effect of PVP concentration on the diameter and its uniformity of electrospun titania nanofibers was pronounced, but the other effects, such as $Ti(OCH(CH_3)_2)_4$ concentration, flow rate and electric field, were relatively negligible especially for the annealed fibers.[15,16] The variation of the solution viscosity and the surface tension as a function of PVP concentration is presented in Fig. 2. The viscosity increased approximately exponentially with increase in PVP concentration. The viscosity was determined to be important for the fabrication of uniform and smooth fibers without beads because the surface tension remained almost constant throughout the experiment.[17] SEM results revealed that the beaded nanofibers having the viscosity less than 59 cP became discontinuous during annealing, as shown in Fig. 3. It is noted that the critical value of the viscosity is likely to be above ~59 cP for the uniform TiO_2

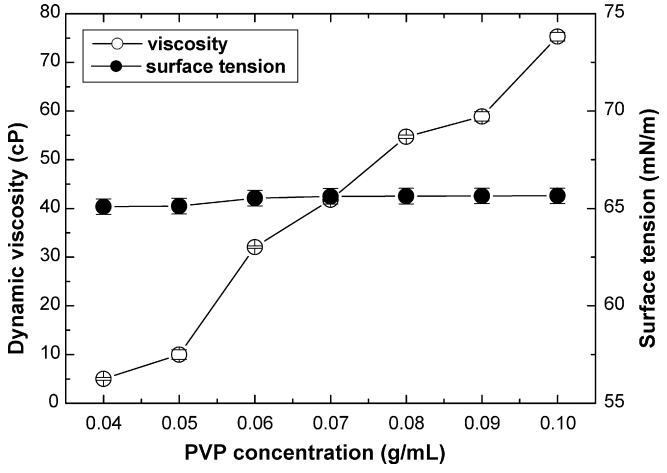

Fig. 2. The variation of the solution viscosity and the surface tension as a function of PVP concentration. Note that the flow rate, the electric field, and the $Ti(OCH(CH_3)_2)_4$ concentration were 0.5 ml/h, 1 kV/cm, and 0.14 g/ml, respectively.

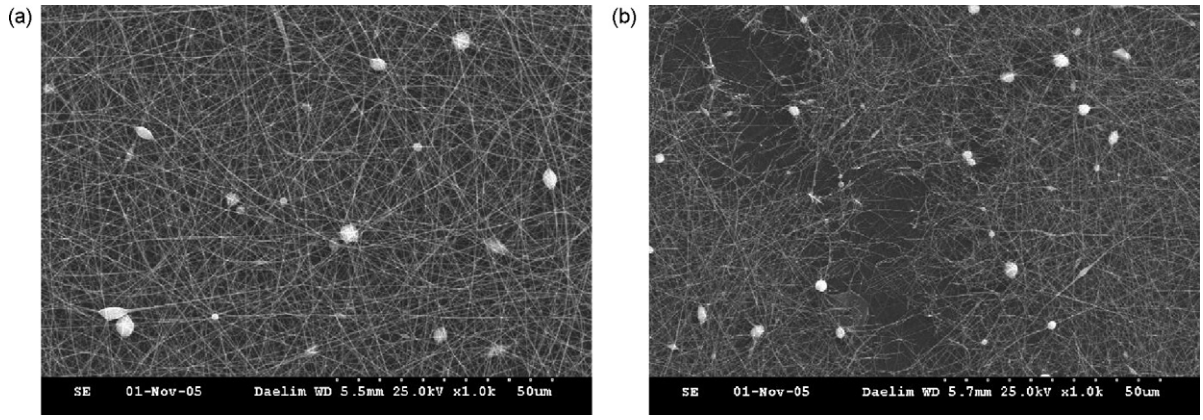

Fig. 3. SEM micrograph of the TiO_2 nanofibers: (a) before and (b) after annealing for 3 h at 500 °C in air. Note that the PVP concentration, the electric field, the Ti concentration, and the flow rate are 0.08 g/ml, 1 kV/cm, 0.14 g/ml and 0.5 ml/h.

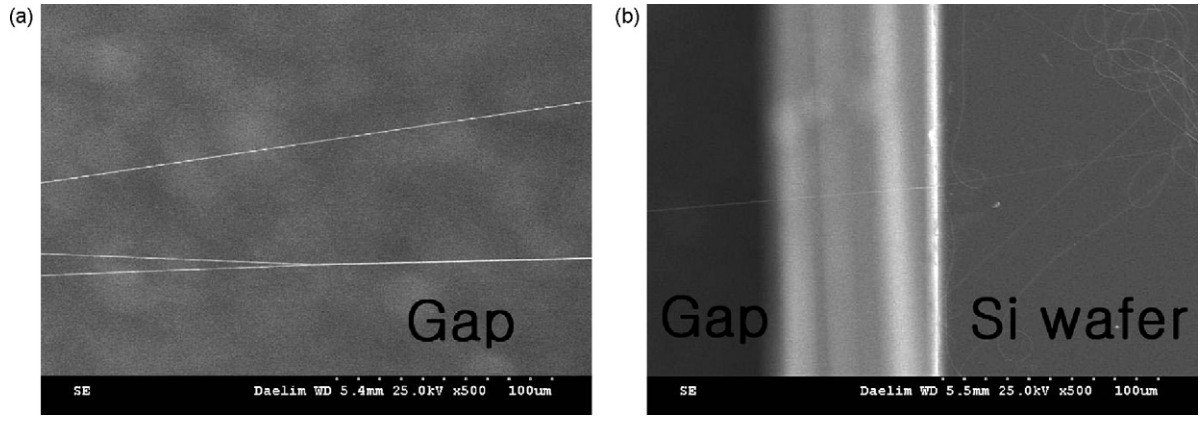

Fig. 4. SEM micrographs of the electrospun fibers across two Si substrates. Note that the TiO_2/PVP nanofibers were stretched across two Si wafer electrodes.

fibers without beads. Uniform and smooth fibers with diameters of 120 ± 10 nm were observed at a PVP concentration of 0.09 g/ml, a $Ti(OCH(CH_3)_2)_4$ concentration of 0.14 g/ml, a flow rate of 0.5 ml/h, and an electric field of 1 kV/cm, respectively. No breakage of the fibers during annealing was found.

The collector was modified by placing two pieces of Si substrates separated by a gap of 1.5 mm to obtain uniaxially aligned fibers. The collection was performed for 3 s. It is reported that the electric field lines in the vicinity of the collector were split into two fractions pointing toward opposite edges of the gap due to the electrostatic forces acting on a charged nanofiber spanning the gap.[13] Also, the stronger electrostatic force will be achieved across the collector spacing with decreasing the gap because Coulomb interactions are inversely proportional to the square of the separation between charges. SEM results (Fig. 4) indicated that the fibers were well ordered across the gap between Si substrates with their longitudinal axes oriented perpendicular to the edges of the gap. Although the directionality of the fibers was improved, the ordering was damaged with increasing the collection time. As the collection time rose (1 min), the curved fibers were visible (Fig. 5).

To obtain a grid structure, a collector consisting of two sets of copper substrates placed by 90° is prepared for biaxial alignment of fibers. SEM images were not clear because the copper substrates were placed on the alumina plate, resulting in the electric charging during the SEM observation. Fig. 6 showed that the directionality of the fibers across the gap (15 mm) was improved significantly even though the gap was 10 times wider than before. Also, no curved fibers were observed.

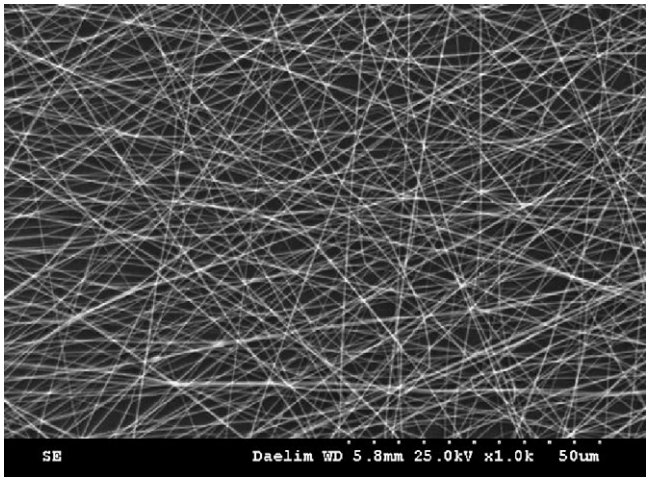

Fig. 5. SEM micrographs of the electrospun TiO_2/PVP fibers. Note that the fibers were electrospun for 1 min.

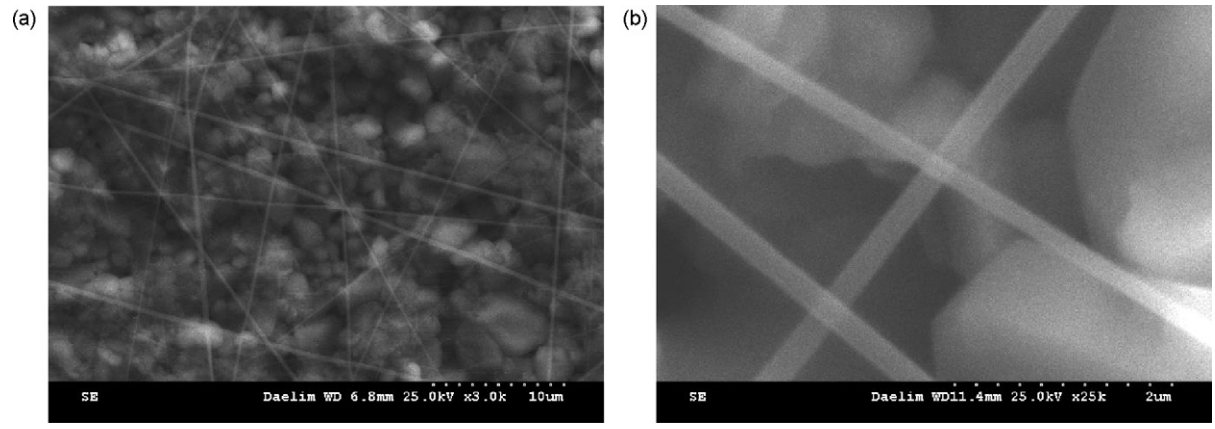

Fig. 6. SEM micrographs of the electrospun TiO_2/PVP fibers with (a) low and (b) high magnification. Note that the fibers were electrospun for 10 s.

The directionality was likely to be improved during the 25 ms interval controlled by the timer. However, it warrants further study.

4. Conclusions

TiO_2/PVP nanofibers were electrospun by varying the collector grounding geometry to improve the axial alignment of fibers. The collector is composed of two pieces of conductive substrates separated by a gap for the uniaxial alignment of fibers (X design). A collector consisting of two sets of substrates placed by 90° (XY design) is also prepared for a grid structure of the fibers. Both collectors show that the charged nanofibers are stretched to span across the gap between the electrodes. Experimental results indicate that the latter is determined to be more effective on the directionality of electrospun TiO_2/PVP nanofibers.

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