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Temperature-induced changes in morphology and structure of TiO_2–Al_2O_3 fibers

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ABSTRACT

Electrospinning of a sol-gel and polymer mixture is used to produce titania-alumina (TiO_2–Al_2O_3) fibers with diameters ranging from 200 to 800 nm. These composite metal-oxide fibers were calcined at various temperatures and their morphology is studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The decrease in the average diameter of the fibers with increasing temperature is observed. Powder X-ray diffraction (XRD) reveals that up to 800 °C the composite fibers have anatase titania structure whereas at 900 °C the fibers exhibit mixture of anatase and rutile phases. It is found that specific surface area decreases as a function of temperature in the 700–900 °C range. The change in phase (anatase-to-rutile) and the increase in crystallite size occur simultaneously. The presence of smaller amount of amorphous alumina in the primarily titania-based structure seems to play the role in stabilizing the anatase phase.

1. Introduction

Titania (TiO_2) nanomaterials can be prepared using different methods and these nanostructures generally have different physical and chemical properties from the bulk material [1]. TiO_2 nanofibers have been successfully prepared using electrospinning by various research groups [2–6]. This method has also been used to fabricate alumina (Al_2O_3) nanofibers [7,8], and composite metal-oxides [9–12]. Mixed or doped metal-oxide nanofibers hold great promise in variety of applications. For example, erbia doped TiO_2 have potential to be used in thermophotovoltaic applications [12] whereas the deposition of gold nanoparticles on electrospun TiO_2 fibers was considered for use in catalysis and chemical sensing [13]. Although the anatase phase has the highest photoactivity among the three titania phases (brookite, anatase, and rutile) [14], the commercial photocatalyst Degussa P25 is the mixed-phase (anatase-rutile) titania [15]. Since the interaction between anatase and rutile phases at interfaces is very likely the source of increased activity, exploring mixed-phase titania materials that could further improve photocatalytic properties is of great interest in applied science.

Alumina-titania fibers, which are the subject of the present study, were previously prepared by a pH-swing method [16] and by our group using electrospinning [11]. The great advantage of electrospinning process is its relative simplicity and the easiness of implementation as the major component of the apparatus is the high-voltage power supply. In our previous and related study on these composite metal-oxide fibers X-ray energy dispersive spectroscopy (XEDS) revealed that the calcined fibers were composed of (in atomic %) 69% O, 27% Ti, and 4% Al [11]. X-ray photoelectron spectroscopy (XPS) showed that the surface elemental composition of the calcined fibers was different from the bulk composition. XPS revealed 18.3% Ti, 13.5% Al, and 68.2% O, indicating that aluminum resides on the surface of the fibers. The application of mixed titania and alumina phases depends on the crystal structure of the composite, its morphology, the degree of crystallinity, and specific surface area. Since there was no significant change in the elemental composition of TiO_2–Al_2O_3 fibers as a function of the temperature, in this study the focus is on the structural, morphological, and specific surface area changes as a function of calcination temperature.

2. Experimental

2.1. Preparation of titania-alumina nanofibers

Aluminum acetate (Aldrich), methanol (Fisher Scientific), and glacial acetic acid (Fisher Scientific) were mixed at weight ratio of 1:15:1, respectively, in order to make the precursor-polymer solution for electrospinning, and the resulting solution was then stirred

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at 333 K for a few hours. Methanol is used because it yields a clear and homogeneous solution. Tetraisopropyl titanate (Du Pont: Tyzor TPT Titanate) was added to this solution at the weight ratio of 0.8:1 and stirred until a homogeneous Ti–Al – polymer mixture was attained. The solution used for electrospinning was obtained after addition of a 2 g polymer solution of polyvinylpyrrolidone (PVP) in ethanol (PVP:ethanol = 1:13 weight ratio) to 1 g of the Ti–Al – polymer mixture. Ethanol is now used instead of methanol for the PVP solution since methanol evaporates faster than ethanol and results in formation of larger fibers. Furthermore, ethanol is an environmentally friendly solvent. The final solution was yellowish in color and transparent. We found that the PVP:ethanol ratio determines whether the mixture electrospins, electrosprays, or fails to form a jet. This mixture was electrospun at a constant flow rate of 20 ml/min via syringe pump with an applied voltage of 20 kV and the tip-to-collector distance of 15 cm. The electrospun fibers were then calcined in a furnace at 700 °C, 800 °C, and 900 °C with a heating rate of 10 °C/min and are held for 1 h at each final temperature. Since increasing the amount of alumina decreases crystallinity of the composite nanofiber structures, changing the amount of alumina with the titania nanofibers is not the subject of the present study.

2.2. Characterization of titania-alumina nanofibers

2.2.1. Scanning electron microscopy (SEM)

All SEM images of as-spun and calcined fibers were taken using Hitachi S – 2460N under the same conditions with 8000 magnification, the voltage of 10 kV, and without coating of the samples. The average thickness of the fibers was obtained directly from SEM images and the results are shown as histograms. Each histogram is generated from 60 measurements.

2.2.2. Transmission electron microscopy (TEM)

A Hitachi H – 7000 transmission electron microscope was used. All images were acquired at magnification of 80 000 with the accelerating voltage of 100 kV. The nanofibers were directly dispersed on the TEM grids without using any solvents. Our TEM system is not equipped with an electron diffraction unit and structural changes will be analyzed using X-ray diffraction measurements.

2.2.3. X-ray diffraction (XRD)and X-ray energy dispersive spectroscopy (XEDS)

A powder X-ray diffractometer (Rigaku D/Max-2000T) operating 40 kV and 40 mA was used for crystal phase determination of the electrospun fibers. XEDS measurements were performed with the SEM system. Cu K_α radiation ($\lambda = 0.154$ nm) is used. Scans from 10 to 70 2-theta degrees have been selected with the step size of 0.05 and scan speed of 0.1^0/min. The elemental composition of the composite nanofibers was analyzed using X-ray energy dispersive spectrometer (XEDS, FEI Quanta 200).

2.2.4. Brunauer – Emmett – Teller (BET)

Specific surface area of the calcined nanofibers was determined by nitrogen adsorption at liquid nitrogen temperature using BET system (NOVA 4200 Quantachrome Instruments). The measurements of the surface area have been repeated several times with the uncertainty of 1 m^2/g and prior to the measurements fibers were outgassed at 300 °C for about 3 h.

3. Results and discussion

Titania (TiO_2) can crystallize in brookite (orthorhombic), anatase (tetragonal), and rutile (tetragonal) phases. Rutile phase is thermodynamically stable whereas brookite and anatase crystal structures convert to rutile titania at elevated temperatures. While anatase titania attracts interest in photocatalytic applications, rutile titania shows promise for some high temperature applications [12] and its presence along with anatase phase appears to improve the photocatalytic properties of titania further. Therefore, diffraction studies are essential for understanding the temperature-induced phase changes.

XRD patterns are displayed in Fig. 1. The as-spun fibers revealed amorphous form. This is the result of the fact that large quantities of polymers are still present in these fibers. The diffraction patterns of composite fibers calcined at 700, 800, and 900 °C are shown in the same Figure and are shifted vertically for clarity. One-hour of calcination at 700 °C results in the formation of anatase titania whose Bragg peaks (101), overlapping (103) + (004) + (112), (200), overlapping (105) + (211), overlapping (213) + (204), and (116) are for simplicity denoted by a single letter A, standing for anatase. Closer inspection at a different scale shows that the brookite (121) peak was at the edge of the detection limit and we leave the possibility that this phase was present in minute amounts at 700 °C. Further calcination at 800 °C for 1 h increases the level of crystallinity of anatase phase as evidenced by sharper features and better resolution of the overlapping peaks. There is no indication of the formation of rutile titania nor alumina phases at 800 °C. It is interesting to compare this transition temperature with that reported in related research on titania nanofibers. For example, the mixture of anatase and rutile phases was observed on titania nanofibers at 600 °C [17,18]. Moreover, even pure rutile titania nanofibers were reported after calcination at 600 °C [2]. Although the absence of alumina signatures in XRD can be explained by the small amount of material present along with relatively high heating rate and relatively small calcinations temperature [7], the absence of rutile structure is interesting and reveals improved stability of anatase phase desirable in applications where anatase phase is preferred. The relatively small amount of amorphous alumina can shift the anatase-to-rutile phase transition to higher temperatures. The mixture of anatase and rutile titania phases is evident in diffraction experiments after calcination at 900 °C. In addition to

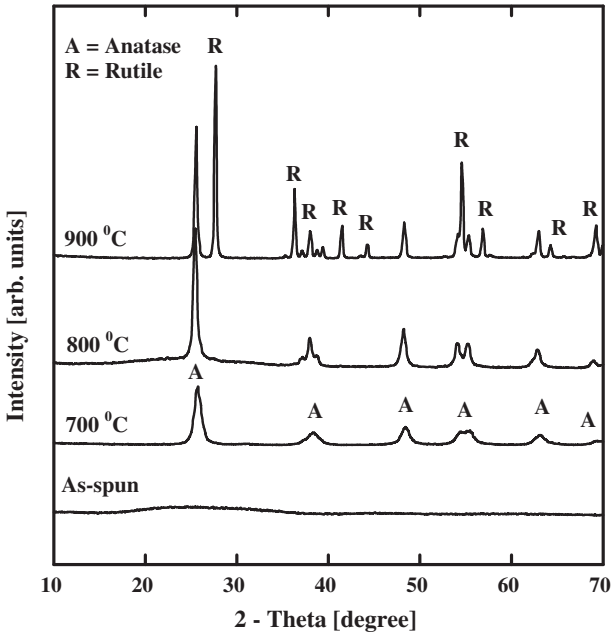

Fig. 1. XRD patterns of as-spun and calcined fibers: as-spun, calcined at 700 °C for 1 h, calcined at 800 °C for 1 h, calcined at 900 °C for 1 h.

anatase Bragg peaks, the rutile features ((110), (101), (200), (111), (210), (211), (220), (002), (310), (301)) are now also present. All rutile peaks are represented with a single letter R, standing for rutile. Since calcination at 900 °C results in the mixture of anatase and rutile the mass fraction, M_f, of rutile structure [19], can be calculated as M_f (rutile) $= I_r/(0.886I_a + I_r)$, where I_a and I_r are the integrated intensities of the anatase (101) and rutile (110) peaks, respectively. For 900 °C fibers M_f (rutile) = 0.63 and M_f (anatase) = 0.37.

The morphology of the as-spun and calcined nanofibers was studied by SEM and TEM. Fig. 2 shows SEM images of as-spun (Fig. 2A), calcined at 700 °C (Fig. 2B), 800 °C (Fig. 2C), and 900 °C (Fig. 2D) fibers. The corresponding diameter histograms (obtained from 60 measurements) are shown in Fig. 3(A–D). The appearance of as-spun composite fibers is smooth due to the amorphous nature as confirmed by XRD measurements. The individual as-spun fibers have very uniform cross-sections with the size in the range of 200–800 nm. Fig. 2B shows morphology of the fibers calcined at 700 °C when polymer is removed. The calcination at 700 °C significantly reduces the average diameter of the fibers and produces a rough surface morphology. The decrease in the fiber diameter is the result of the removal of polymer and conversion from amorphous to anatase phase. At 700 °C the fibers exhibit only anatase titania phase as confirmed by diffraction measurements. The fibrous structure of the as-spun composite is preserved in the process of calcination. Further calcinations above 700 °C continue to reduce the fiber diameters, consistent with the change in the size of the crystallites. Fig. 2D shows the fibers with mixed anatase and rutile phases.

The crystallite size of the composite titania-alumina nanofibers has been estimated using the Scherrer equation which relates the full width at half maxima (FWHM), W, of the most intense peak to the angle of incidence, θ, via $S = c\lambda/W\cos\theta$, where S is the crystallite size, c is the Scherrer constant whose value depends on the shape of the particles (between 0.9 and 1.2), and λ is the wavelength of the incident X-rays. The spherical shape was assumed and the Scherrer constant was set to $c = 1$. All three calcination temperatures produce the fibers with anatase titania phase and the size of the crystallites increased as a function of temperature from 11 nm to 18 nm in going from 700 °C to 800 °C, and from 18 nm to 26 nm in going from 800 °C to 900 °C. The values are obtained from the most intense Bragg peak denoted (101). The change in phase (anatase-to-rutile) and the increase in crystallite size occur simultaneously. The crystallite size of rutile titania, observed at 900 °C, was calculated from the (110) peak. The average crystallite size of rutile titania was estimated to be 32 nm. It has also been proposed in a related study on electrospun TiO_2 nanofibers that the grain growth could be significantly enhanced by the transformation of phase from anatase to rutile due to the higher atomic mobility induced by bond braking during the transformation [20].

TEM measurements are used to study the morphology of the fibers in more details. Fig. 4 shows as-spun fibers (Fig. 4A), and those calcined at 700 °C (Fig. 4B), 800 °C (Fig. 4C), and 900 °C (Fig. 4D). Calcination at 700 °C significantly changes the morphology of the fibers. Further increase in calcination temperature reveals crystallites growth and how anatase-to-rutile transformation modifies the fiber morphology. The fibers calcined at 900 °C appear to be composed of particles 5–10 times smaller than the diameter of the fiber. Unlike as-spun composite fibers, all calcined fibers exhibit rough surface morphology and some voids between particles are apparent. The diameter of each fiber appeared uniform in these experiments. XRD results suggest that the particles seen in the TEM images correspond to anatase (Fig. 4B and C) and to anatase and rutile titania (Fig. 4D).

Specific surface area measurements are performed on fibers calcined at 700, 800, and 900 °C. The surface area decreases as the calcination temperature increases from 700 to 900 °C. In particular, at 700 °C the specific surface area was 33.8 m^2/g and decreased to

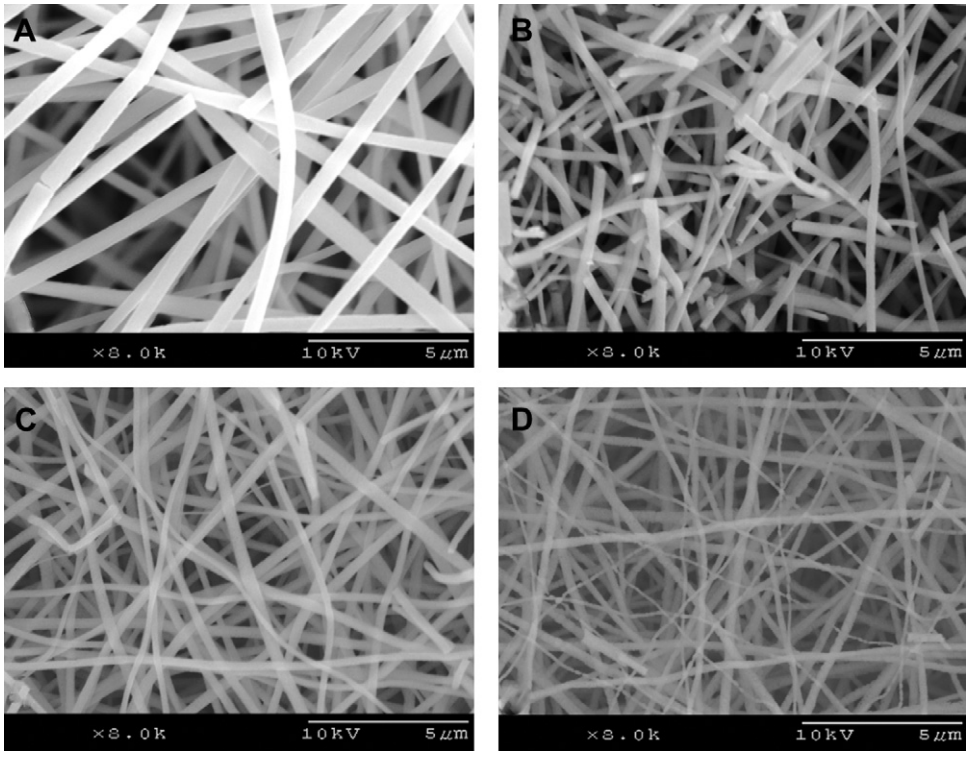

Fig. 2. SEM images of as-spun and calcined fibers: (A) as-spun, (B) calcined at 700 °C for 1 h, (C) calcined at 800 °C for 1 h, (D) calcined at 900 °C for 1 h.

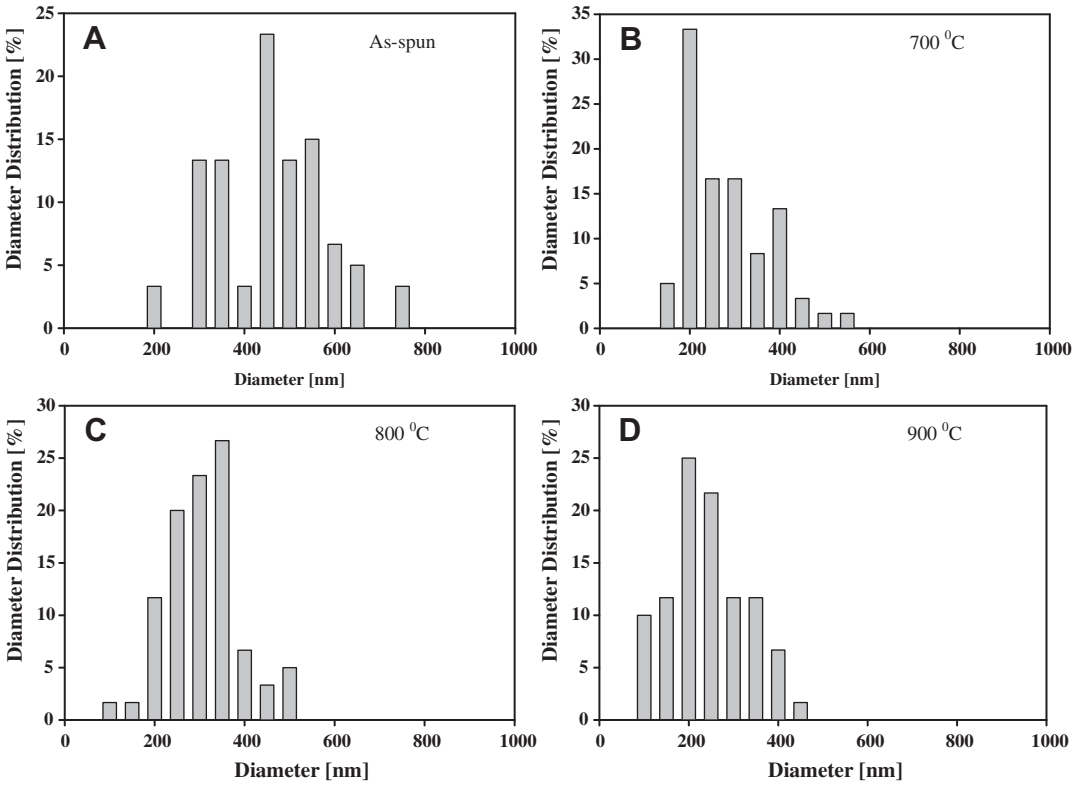

Fig. 3. Histograms of as-spun and calcined fibers showing the diameter distribution: (A) as-spun, (B) calcined at 700 °C for 1 h, (C) calcined at 800 °C for 1 h, (D) calcined at 900 °C for 1 h. Values are obtained from SEM.

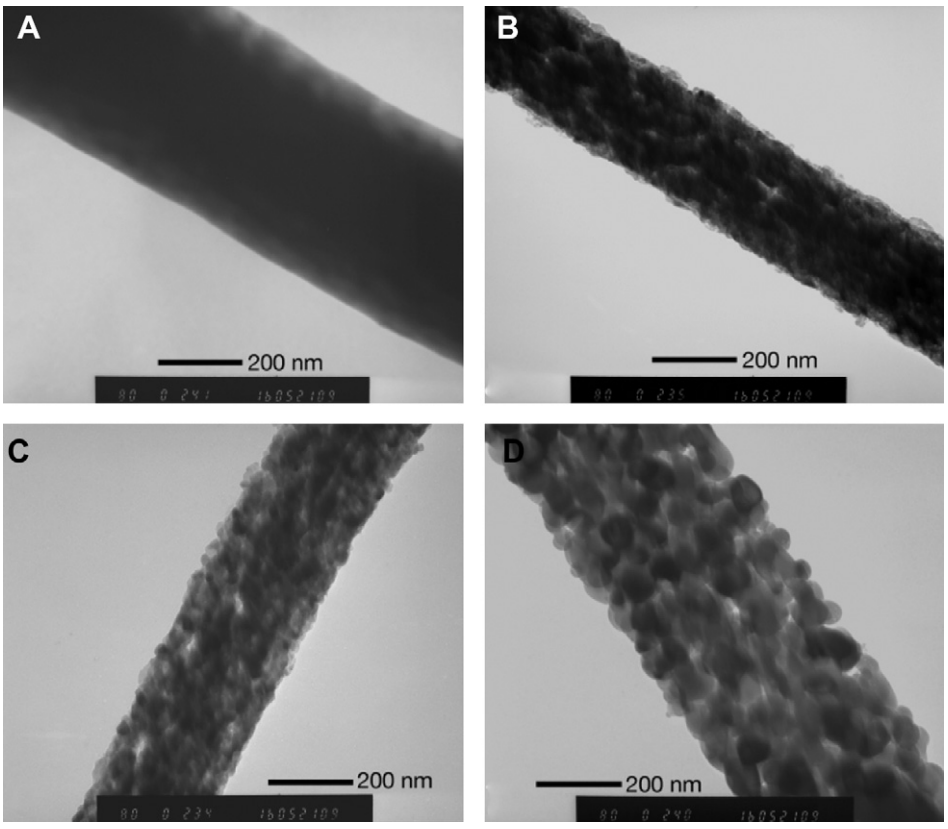

Fig. 4. TEM images of as-spun and calcined fibers: (A) as-spun, (B) calcined at 700 °C for 1 h, (C) calcined at 800 °C for 1 h, (D) calcined at 900 °C for 1 h.

27.2 m^2/g at 800 °C and further decreased to 10.1 m^2/g at 900 °C when anatase and rutile phases co-exist. This trend is consistent with other related studies on titania nanoparticles [21]. The optimal surface area can, therefore, be achieved by selecting the calcination temperature.

4. Conclusions

Composite titania-alumina nanofibers were successfully prepared by electrospinning a sol-gel and polymer mixture. Electron microscopes (SEM and TEM) were used to study temperature-induced morphological changes whereas X-ray diffraction measurements were employed to monitor the corresponding changes in the crystal structures. The fibers were predominantly made of titania. Calcination at high temperatures (700, 800, and 900 °C) resulted in the change of morphology of electrospun fibers driven by the gradual increase in the crystallite size with increasing temperature and the phase transition from anatase to rutile. Fibers calcined at 800 °C for 1 h showed no evidence for the presence of rutile phase implying delayed anatase-to-rutile transition desirable for applications where improved thermal stability of anatase phase is desirable. The specific surface area of the calcined fibers decreased as the temperature increased above 700 °C. The simplicity of the electrospinning method is its great advantage in preparing the composite metal-oxide nanofibers. By varying the preparation conditions one can vary the physical and chemical properties of the electrospun metal-oxide nanofibers to target various applications.

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