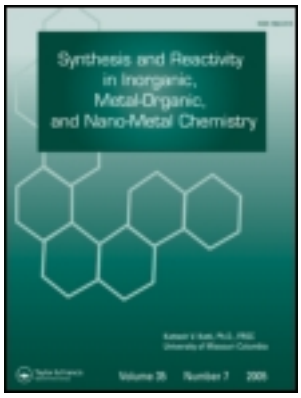

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Synthesis and Characterisation of Zirconium Oxide Nanofibers by Electrospinning

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Nanometer-sized zirconium oxide (ZrO_2) fibers with diameters about 200 nm have been synthesized by calcination of the zirconium oxide/poly(vinyl acetate) (PVAc) composite nanofibres prepared by sol-gel processing and electrospinning technique. The general morphology of the nanofibers has been studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The crystalline phase evolution as a function of calcination temperature was studied by X-ray diffraction patterns (XRD) of the nanofibers, which showed that the samples after calcination at 500°C and 750°C showed the presence of tetragonal phase along with some traces of monoclinic zirconium oxide. After calcination at 1000°C, only monoclinic phase was identified in the XRD patterns. The formation of pure zirconium oxide was further confirmed by FT-IR spectra.

Keywords zirconium oxide, scanning electron microscopy (SEM), X-ray diffraction (XRD), electrospinning

INTRODUCTION

One-dimensional (1D) nonostructural metal oxides and related materials have been a subject of intense research because of their potential applications in many fields that include electronics, photonics and sensing.[1] A number of synthetic methods for generating nanoscale wires, belts and tubes of various metal oxides have been demonstrated, notable examples include carbothermal reduction,[2] thermal evaporation,[3] metallo-organic decomposition,[4] and anodic oxidation.[5] New strategies are still being developed. Nowadays, electrospinning technique has been successfully employed in the preparation of metal oxide fibers such as, zinc oxide,[6] vanadium pentoxide,[7] cobalt oxide,[8] nickel oxide,[9] copper oxide,[10] titanium oxide,[11] magnesium titanate,[12] nickel titanate,[13] etc. Electrospun nanofibers have approximately 1 to 2 orders of magnitude more surface area than that found in thin films.[14]

Zirconium oxide or zirconia (ZrO_2) is an important technological material that can show a visible photoluminescence (PL) under an excitation by UV light. The excellent optical, mechanical, electrical, chemical and photochemical properties of this material made it suitable for different applications such as interferometric filter,[15] coating material,[16] catalysts[17] and sensors.[18] Though several reports are available on the preparation of zirconium oxide films[16,18] and nanocrystalline powders,[17–19] there seems to be no report on the preparation and characterization of zirconium oxide nanofibers. Hence, for the first time, we present herein that nanometer-sized zirconium oxide fibers can be conveniently prepared by electrospinning a composite solution that contains zirconium oxide precursor sol and PVAc followed by high temperature calcination of the inorganic/organic composite nanofibers.

EXPERIMENTAL

Zirconium isopropoxide and *N*, *N*-dimethyl formamide (DMF) were purchased from Aldrich and used without further purification. PVAc (Mn = 500,000) was obtained from Celanase Ltd.

Preparation of the Nanofibers

Zirconium oxide sol was prepared as described below using zirconium isopropoxide as the precursor. Then, 7.5 g of zirconium isopropoxide was dissolved in 20 g of absolute ethanol and 0.15 g of nitric acid and 0.21 g of hydrochloric acid were

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added and stirred for 4 h. PVAc (18 wt%) solution was prepared in DMF. The solution required for electrospinning was prepared by stirring the zirconium oxide sol and PVAc (18 wt% in DMF) in the ratio of 0.75:1 (w/w), for 6 h at room temperature. The viscous solution thus obtained was placed in a hypodermic syringe. The positive terminal of a variable high voltage power supply was attached to a copper wire inserted into the solution in the syringe, whereas the ground iron drum covered with an aluminium foil served as counterelectrode. A schematic diagram of the electrospinning process was given in Figure 1. The distance between the tip of the syringe and collector was 16 cm. The syringe was placed at an angle of 20° to horizontal in order to get uniform flow of the solution. When the voltage applied between the two electrodes reached 15 kV, dry, web of composite nanofibers with several centimeter length accumulated on the surface of the aluminium foil. The zirconium oxide/PVAc composite nanofibers deposited were collected and calcinated in air at high temperatures for 4 h to get pure zirconia nanofibers.

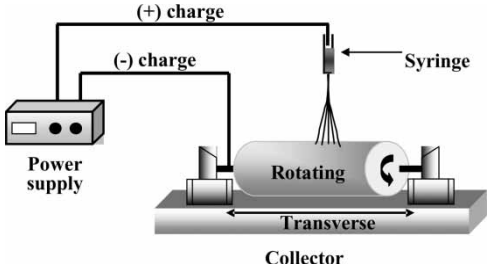

FIG. 1. A schematic diagram of electrospinning process.

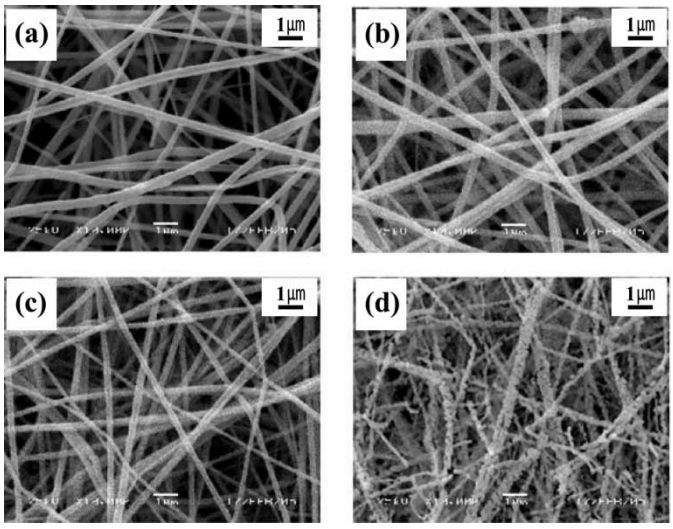

FIG. 2. SEM images of zirconium oxide nanofibers: (a) as-synthesised zirconium oxide/PVAc composite fibers, (b) fibers calcinated at 500°C, (c) fibers calcinated at 750°C and (d) fibers calcinated at 1000°C.

Characterisation of the Nanofibers

SEM images of the samples were recorded by JEOL GSM-5900 scanning electron microscope. Tapping mode AFM images were obtained from Nanoscope(R)-III A instrument. Powder X-ray diffraction patterns of the fibers were obtained from Rigaku X-ray diffractometer using Cu-Kα radiation in the 10–70 2θ values. FTIR spectra of the samples (as pellets in KBr) have been recorded in Bio-Rad Win instrument. The as-synthesised inorganic/organic composite fibers were calcinated for 4 h at different temperatures ranging from 500°C to 1000°C at a heating rate of 2°C/min in air.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

The nanostructure of the fibers was analysed by scanning electron microscopy (SEM). Figure 2 shows the SEM images of the various nanofiber samples. The as-synthesised zirconium oxide/PVAc composite nanofibers were found to have smooth, uniform surfaces with varying diameters in the 400–500 nm range (Figure 2a). The fibers obtained after calcination at 500°C appeared to have the rough surface owing to crystallization of zirconium oxide at this temperature with cylindrical morphologies (Figure 2b). But the samples obtained after calcination at 750°C showed about 30–40% decrease in their diameters, which is due to the decomposition and removal of PVAc component that played the role as a template for fiber formation during electrospinning process (Figure 2c). However, it can be seen from the SEM images of the nanofibers after calcination at 1000°C, that their morphology has changed to one where the fibers appear to consist of linked particles or crystallites (Figure 2d).

Atomic Force Microscopy

Atomic force microscopy (AFM) was used to obtain qualitative information about the surface morphology of the nanofibers. Figure 3 represents the AFM images and the height profiles of the corresponding as-synthesised zirconium oxide/PVAc composite nanofibers marked on the images. It can be seen from the AFM images that the as-synthesised zirconium oxide/PVAc composite fibers have uniform, smooth surfaces with cylindrical structure and their diameter ranges from 400–500 nm as found in the SEM images. Our attempt to obtain the AFM photographs of the calcinated samples went unsuceessful due to the surface roughness resulted from crystallization of zirconium oxide.

X-ray Diffraction Patterns

The crystalline phase evolution of zirconium oxide nanofibers has been examined by XRD measurements. Figure 4 shows the XRD patterns of various ZrO2 samples. Zirconia has two crystalline phases, tetragonal and monoclinic.[20] Amorphous behaviour was observed in the XRD of the

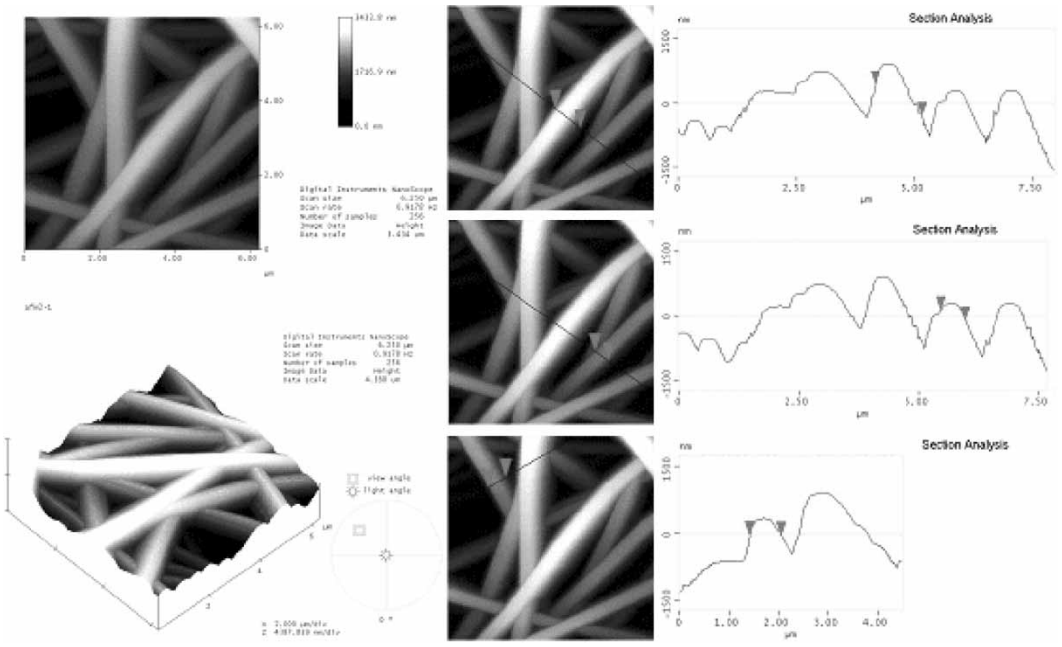

FIG. 3. 1-dimensional and 3-dimensional AFM images of as-synthesised zirconium oxide/PVAc composite fibers and corresponding height profiles.

as-synthesised ZrO_2/PVAc composite nanofibers (Figure 4a). The samples obtained after calcination at 500 °C exhibits the diffraction peaks centered at 30.35° $(1,0,1)_t$, 35.30° $(0,1,1)_t$, 50.50° $(2,1,1)_t$ and 60.40° $(1,1,2)_t$, and are characteristics of the tetragonal zirconium oxide suggesting that the sample present mainly in the metastable tetragonal phase (Figure 4b). This result is in accordance with the data reported in the case of nanocrysalline zirconia.[19] However, small peaks centered at 24.60° $(1,1,0)_m$ 28.40° $(-1,1,1)_m$ revealed the coexistence of some content of monoclinic crystalline phase also.[19,20] The diffraction peaks corresponding to the monoclinic zirconium oxide phase became more sharper and intense when the calcination temperature was increased to 750°C showing the presence of both tetragonal and monoclinic phases considerably (Figure 4c). This indicates the gradual transformation of the metastable tetragonal phase to the monoclinic structure. In the XRD pattern of the nanofibers calcinated at 1000°C (Figure 4d), only monoclinic phase was observed as indicated by the absence of the characteristic tetragonal peak at 30.35°. The diffraction peaks corresponding to the tetragonal and monoclinic phases were well matched with database in JCPDS (Card No. 89-2843) and earlier reports for zirconium oxide nanocrystals and films.[19,20]

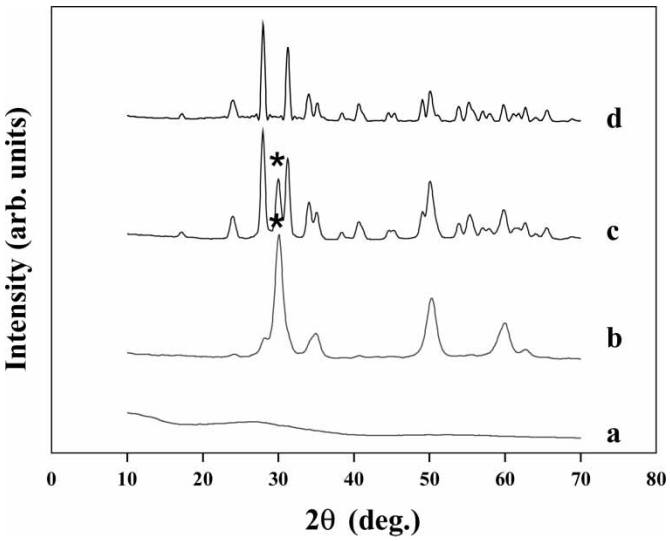

FIG. 4. XRD patterns of zirconium oxide nanofibers (a) as-synthesised zirconium oxide/PVAc composite fibers, (b) fibers calcinated at 500°C, (c) fibers calcinated at 750°C and (d) fibers calcinated at 1000°C (∗denotes the diffraction peak characteristic of tetragonal zirconium oxide).

FT-IR Spectral Study

In order to confirm the formation of pure zirconium oxide nanofibers after calcination at high temperature with the complete removal of poly(vinyl acetate) templates, we recorded the FT-IR spectrum of the various nanofiber samples. The FT-IR spectrum of the as-synthesised inorganic/organic hybrid nanofibers (Figure 5, curve a) showed some strong absorptions in the region 1000 to 1750 cm^{-1}, corresponding to the stretching and bending vibrations of PVAc molecule. After calcinations at 500°C, the intensity of those peaks due to PVAc were decreased or almost disappeared, indicating the removal of PVAc molecules from the fibers, and new peaks appeared around 750 cm^{-1}, 550 cm^{-1} and 430 cm^{-1} due to the formation of zirconium oxide (Figure 5, curve b).

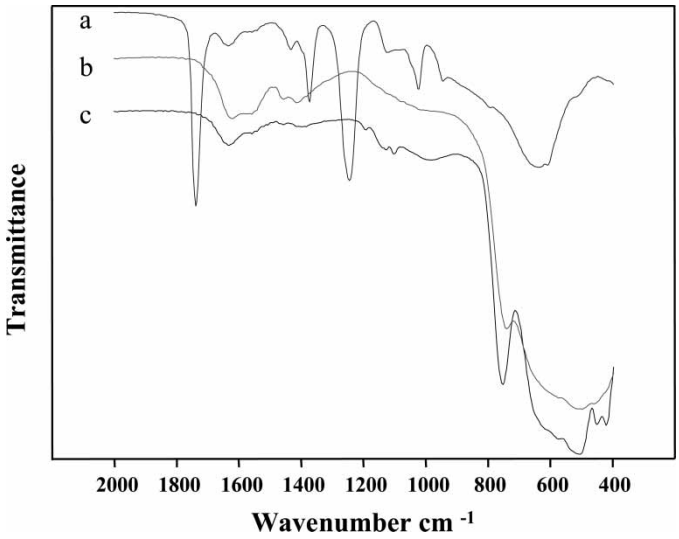

FIG. 5. FT-IR spectra of zirconium oxide nanofibers (a) as-synthesised zirconium oxide/PVAc composite fibers, (b) fibers calcined at 500°C and (c) fibers calcined at 750°C.

The formation of pure zirconium oxide is indicated by the IR spectra of the samples calcinated at 750°C, which displayed intense peak at 520 cm^{-1} and at 750 cm^{-1} (Figure 5, curve c) assigned as due to Zr-O stretching of zirconium oxide.[21] In addition, the disappearance of the absorptions corresponding to the PVAc molecule indicated the complete removal of them at this temperature and the fibers formed were consisting of only zirconium oxide.

CONCLUSION

Pure zirconium oxide nanofibers with about 200 nm diameter were prepared by electrospinning technique. The surface morphology of the fibers has been studied by scanning electron microscope (SEM) and atomic force microscopy (AFM). The observed X-ray diffraction patterns (XRD) of the fibers showed the presence of both tetragonal and monoclinic phases after calcination at 500°C and 750°C. However, the samples obtained after calcinations at 1000°C, showed the presence of only monoclinic phase in the XRD patterns. The formation of pure zirconium oxide was also confirmed by FT-IR spectra.

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