ORIGINAL PAPER

Mechanical properties of titania nanofiber mats fabricated by electrospinning of sol–gel precursor

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Abstract Flexible mats of titania fibers are prepared by calcination of electrospun polyvinylpyrrolidone fibers containing titanium isopropoxide precursor. Structural investigation of the calcinated nanofibers by X-ray diffraction (XRD) and electron diffraction (ED) combined with the morphologies by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show the titania fibers, with an average diameter of 180 nm, were comprised of anatase and rutile crystals. The mechanical, chemical and thermal properties of the titania fiber mats are further investigated by the techniques of Instron mechanical tester, thermogravimetric analyzer (TGA), and Fourier transform infrared spectroscopy (FT-IR). The titania fiber mat prepared in this method exhibited a significant flexibility with 461 MPa Young's modulus.

Keywords Titania · Nanofibers · Electrospinning · Flexibility

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1 Introduction

Titania (titanium dioxide, TiO_2) is an abundant and important ceramic material having strong oxidizing characteristics, excellent chemical stability, good corrosive resistance, and competitive cost effectiveness. Owing to its physical properties, titania has been widely used in industry for decades as a pigment due to its lack of color, a gas sensing active material at high temperature, an electrode in dye sensitized solar cells, and a heterogeneous photocatalyst for the degradation of contaminants in air and water [1–3]. Titania can also act as an N-type semiconductor because of oxygen deficiency [4].

Most of the physical properties of titania mentioned above can be enhanced by increasing its surface area per unit mass, and unique properties can be enhanced when the size of the titania structure decreases into nanometer length scale with respect to their bulk counterparts [5, 6]. From this aspect, many material scientists and engineers have fabricated titania nano-structures through various methods, such as sol–gel processing, self-assembling, strong alkali treatment, electrospinning, and thermal evaporation methods [7–12].

Among these techniques, electrospinning is one of the simplest and most versatile methods for fabricating polymeric or composite fibers and has been applied to expand the use of titania and to enhance its physical properties. In the electrospinning process, a jet of polymer and sol–gel mixture is launched from a droplet at the end of a small nozzle by action of an electric field. The jet stretches and elongates to form continuous fibers with nanometer diameters [13]. Nanometer-sized titania fibers with large surface area per unit mass can enhance electrical, physical, and chemical properties with respect to their bulk counterparts [5, 14].

In addition to TiO$_2$, other metal oxide nanofibers or nanotubes such as ZnO, SiO$_2$, Ga$_2$O$_3$, CuO, SnO, NiO, and mixtures of metal oxides, NiO/ZnO and Pt/Al$_2$O$_3$ have been successfully prepared by this process [15–17]. In order to fabricate inorganic nanofiber mats, polymer nanofiber mats containing metal precursor are first prepared by electrospinning. The prepared polymer nanofiber mats are converted to metal oxide nanofibers by heating the mats in air to oxidize the composite polymer and sol–gel precursors. However, the metal oxides fibers produced by this technique can be brittle, thus limiting their usefulness. Accordingly, there is a need to develop fabrication methods for flexible ceramic nanofibers. Up to now, there are few reports on fabricated flexible titania fibers [18, 19]. To evaluate the mechanical properties of the ceramic or polymer/ceramic composite fibers, a nanometer scale three-point bending test using atomic force microscopy (AFM) was applied [20, 21]. The measurement of mechanical properties of ceramic nanofibers is a challenge. To the best of our knowledge no literature documents the measurement of mechanical properties of TiO$_2$ fiber mats instead of the individual TiO$_2$ fibers.

In this paper, polyvinylpyrrolidone (PVP) and titania precursor were electrospun and subsequently calcinated at 700 °C to titania fibers. X-ray diffraction (XRD) and electron diffraction (ED) of the titania fibers indicate they consist of anatase and rutile crystals. The morphologies of the prepared titania fibers were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The chemical, physical and mechanical properties were also investigated by the combined techniques of thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and an Instron mechanical tester. The mechanical property measurements of the titania fiber mats clearly indicate that the titania fiber mats prepared in this method exhibit an excellent flexibility. It is noteworthy that most of ceramic fibers are brittle and/or powdery after the calcination process. Since the produced titania fiber mats are tough and bendable, these flexible titania nanofibers can handled without any difficulties, which is advantageous for using these titania fibers in practical applications.

2 Experimental procedures

A 7 wt% solution of polyvinylpyrrolidone (PVP, MW: 1,300,000 g/mol, Aldrich) in ethanol (AAPER alcohol) was prepared, and titanium isopropoxide (Aldrich) and acetic acid (Aldrich) were added into this solution in the weight ratio of 6.7:1:2, respectively. The mixture was placed in an ice-water bath for 10 min. The yellowish solution was drawn into a plastic syringe with a 21 gauge stainless steel needle. The needle was charged to 20 kV using a power supply (Gamma High Voltage Research Inc.) and the mixture was pumped at a flow rate of 30 µL/min to the tip of the needle using a syringe pump (World Precision Instruments SP1011). The needle was positioned 15 cm above a grounded collector. A jet of the polymer solution launched from the needle tip and collected on the grounded surface. The collected polymer composite fibers were heated in air atmosphere to 275 or 700 °C at a rate of 4 °C/min and maintained at that temperature for 2 h.

The surface morphology of the electrospun fibers was observed by scanning electron microscopy (SEM, JEOL Ltd., JSM 5310, Japan). The thermal stability of the fibers was measured using thermogravimetric analysis (TGA, Perkin Elmer Inc., Pyris 1 TGA, USA) starting with the polymer composite fibers in an air atmosphere and heated at a rate of 10 °C/min. The vibrational spectra of the ceramic fibers were measured using Fourier transform infrared spectroscopy (FT-IR, ABB Bomen MB100 Spectrometer, Canada).

The phase identification and crystallinity was obtained by using a wide angle X-ray diffraction (XRD, Rigaku, Japan) in the reflection mode with Cu-Kα radiation over Bragg 2θ-angle ranging from 10 to 80°. The high resolution images and selected area electron diffraction (SAED) patterns were obtained with transmission electron micrograph (TEM, JEOL JEM-2010, Japan) at 200 kV. For TEM measurements the calcinated fiber samples were prepared by suspending the fibers in ethanol in a sonication bath for 10 min. A drop of the sonicated sample suspension was allowed to dry on a copper grid coated with a carbon film.

The photographs of the fiber mats were taken using a common digital camera to demonstrate the excellent flexibility of the titania nanofiber mats. Using an Instron mechanical tester (LLOYD instruments, LR5K plus, UK) in tensile mode, mechanical properties of the as-spun polymer mats and the calcined titania fiber mats were measured. The specimen thicknesses were measured using a digital micrometer with a precision of 1 µm. The extension rate was 5 mm/min at room temperature and seven specimens with dimensions of 3.5 mm × 40 mm (width and length) were tested and averaged for each fiber mat.

3 Discussion of results

Figure 1a shows an SEM image of electrospun PVP and titanium isopropoxide composite fibers before heating. The nanofibers are randomly distributed and the average diameter of fibers is about 500 nm. The calcination of these fibers at 700 °C for 2 h yielded ceramic fibers with an average diameter of about 180 nm, as shown in Fig. 1c.

The reduction of nanofiber diameter after calcination could be due to the loss of PVP and the crystallization of titania. To test this hypothesis, the electrospun polymer fiber mats were also heated at 275 °C, which resulted in a mat of fibers with an average fiber diameter of 270 nm as shown in Fig. 1b. As can be observed from the images in Fig. 1b and c the heated fibers retain the continuous fiber structures and smooth surfaces of the template polymer fibers.

The calcination of fibers to 700 °C was quantitatively measured by TGA analysis. The polymer or ceramic fibers
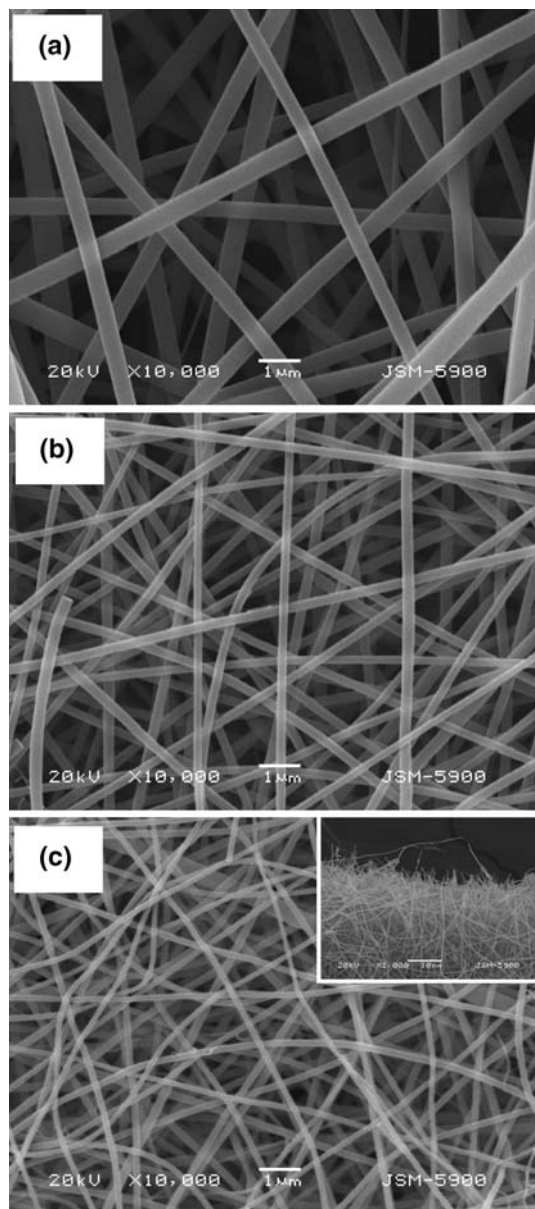

Fig. 2 The TGA and DTA curves for composite polymer fibers (*a*, *b*) and TGA curve for titania fibers calcined at 700 °C (*c*)

Fig. 1 SEM images of composite polymer fibers (**a**), fibers heated to 275 °C (**b**), and fibers calcined at 700 °C for 2 h (**c**). The lower magnification of the inset image in (**c**) shows the fibers are continuous up to the edge of the sample where the sample was cut to fit onto the SEM grid
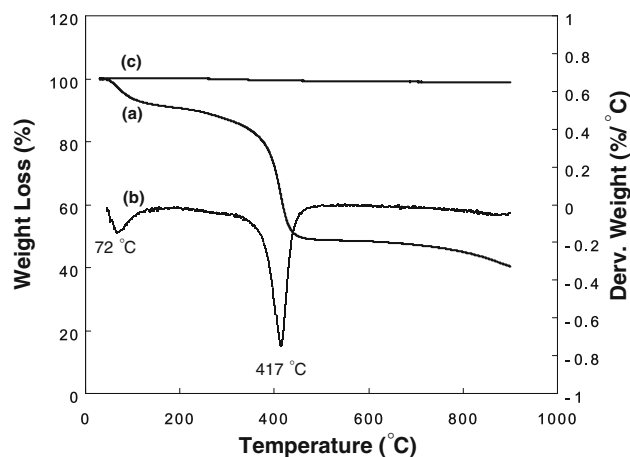
were heated from room temperature to 700 °C at the same heating rate. Figure 2 presents three curves. Curves (a) and (b) show the TGA results for heating of the polymer fibers prior to calcination. Curve (a) shows the change in mass with temperature and curve (b) shows the derivative of curve (a). The derivative curve shows two exothermic peaks at 72 and 417 °C, which indicate the loss of solvent such as water, ethanol, carbon dioxide, and the degradation of PVP polymer. Curve (a) shows the weight losses at 275 and 700 °C were 10 and 53%, respectively which correspond well with the reduction of fiber diameters shown in Fig. 1 after heating to the same temperature. Curve (c) shows negligible change in mass when fibers previously calcined to 700 °C are heated from room temperature to 700 °C. This clearly shows that after calcination at 700 °C for 2 h there is no more polymer to oxidize when heated again.

FT-IR analysis is used to determine the chemical compositions and structures of the fibers. Figure 3 shows the spectra of polymer fibers prior to calcination (curve a), fibers heated to 275 °C (curve b), and fibers calcined at 700 °C (curve c). The FT-IR spectra of polymer fibers (a) and the fibers heated to 275 °C (b) have bands at 1,458 cm^{-1} corresponding to C–H vibration, at 1,292 cm^{-1} for C–C stretching, at 1,681 cm^{-1} C=O stretching and vibration, and at 1,033 cm^{-1} for C–N stretching and vibration [22, 23]. These results clearly indicate that the PVP polymer remains in the fibers heated at 275 °C for 2 h, which agrees well with the TGA results. Curve (c) shows the C–H, C–C, C=O, and C–N vibrational bands observed in curves (a) and (b) are completely absent in the FT-IR spectrum of the fibers calcined at 700 °C for 2 h. Curve (c) shows an emerging a broad band at 775 cm^{-1}, which belongs to the vibrations of Ti–O in titania [24]. Based on the TGA and FT-IR we conclude that calcination of the
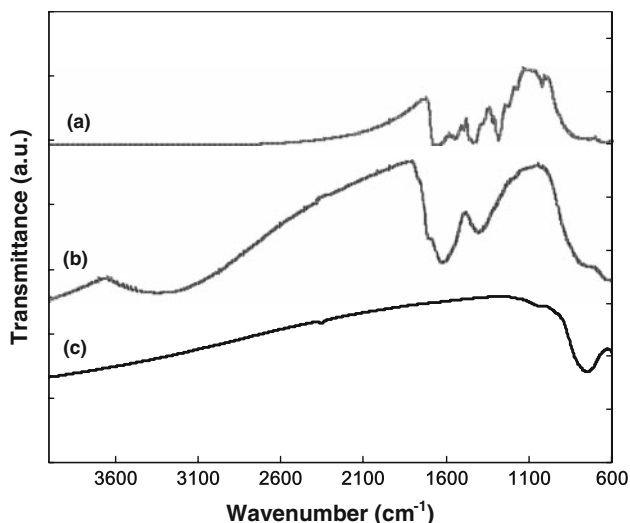
Fig. 3 FT-IR spectra for as-electrospun composite polymer fibers (*a*), fibers heated to 275 °C (*b*), and titania fibers calcined at 700 °C (*c*)

polymer fibers at 700 °C for 2 h essentially removes all of the polymer and solvents from the fibers.

To determine the crystal phases of the titania in the fibers measurements using wide angle XRD were carried out. XRD patterns for the polymer fibers prior to heating, the fibers heated to 275 °C, and the fibers calcined at 700 °C are plotted as curves (a), (b), and (c) respectively in Fig. 4. Over all the XRD patterns of the polymer fibers and the fibers heated at 275 °C do not differ significantly. The strong and broad amorphous halo at $2\theta = 20°$ in curve (a)
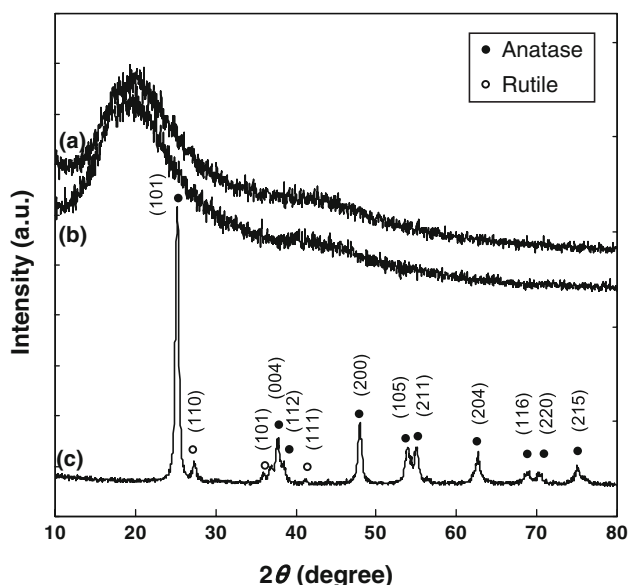

Fig. 4 XRD for as-electrospun composite polymer fibers (*a*), fibers heated to 275 °C (*b*) and titania fibers calcined at 700 °C (*c*)

is shifted to a lower angle of $2\theta = 19.5°$ in curve (b) which should be related to the evaporation of the solvents observed in the TGA analysis (Fig. 2). The XRD pattern of fibers calcined at 700 °C in curve (c) exhibits many sharp diffractions between $2\theta = 20°$ and 80° and there is no trace of amorphous halos as observed in curves (a) and (b). The detected diffractions at 2θ-angles of 25.3, 37.8, 38.6, 48, 54.1, 55.2, 62.7, 69.3, 70.6 and 75.2° can be respectively assigned as (101), (004), (112), (200), (105), (211), (204), (116), (220) and (215) Miller indices based on the anatase titania crystalline structure. In addition to these diffraction, there were diffractions at $2\theta = 27.4$, 36.5 and 41.6° which belonged to rutile titania crystalline structure planes of (110), (101), and (111), respectively. Similar XRD experiments of the calcinated nanofibers were reported by Ramakrishna and coworkers by varying calcination temperatures [25]. They found that the calcinations at 500 °C only provided anatase crystalline form while above 575 °C rutile crystalline form started to be generated. Their results agreed well with our XRD results.

The morphology within the calcinated nanofiber was investigated by bright-field TEM. As shown in Fig. 5a and higher magnification in Fig. 5b, the average diameter of the titania fiber is about 180 nm, which agrees with the SEM observations. The TEM images show the titania fibers consist of two different crystal phases. As indicated in Fig. 5c, SAED of calcinated fibers match well with the XRD results in Fig. 4c. A specific particle in a fiber was magnified by HR-TEM and its bright-field image is shown in Fig. 5d. The inset of Fig. 5d is the Fourier transformed diffraction pattern from the area of Fig. 5d marked with the square, which is also matches well with the titania crystalline structure [25]. As shown in Fig. 5, the calcined nanofiber consisted of TiO_2 particles with less than 15 nm. Smaller grains have greater ratios of surface area to volume. It is known that strength can be enhanced by increasing the ratio of grain boundary to dislocation [26, 27]. During the calcination process, TiO_2 crystallites are grown by transforming the amorphous phase within the electrospun nanofibers In future work a more systematic study should be carried out to find mechanisms and effect of grain size and grain boundary.

The photos in Fig. 6 show all of the fiber mats are self-supporting. The photo in Fig. 6a is that of the polymer fiber mat, 6b is of the mat heated to 275 °C, and 6c is of the mat calcined at 700 °C. The inserted photographs show these mats held with tweezers and demonstrate their flexibility even after the calcination process. Quantified measurement of the flexibility of the mats is left for future work. Xia and Li [8] studied free standing anatase titania fiber mats calcined at 500 °C. In our study, the fiber mat calcined up to 700 °C has a mixture of anatase and rutile titania as a flexible mat.

Fig. 5 TEM images of titania nanofibers (**a**, **b**), selected area electron diffraction (**c**) and HR-TEM (**d**) after calcination at 700 °C. The *inset* of **d** is the Fourier transformed diffraction image of the square area marked in **d**
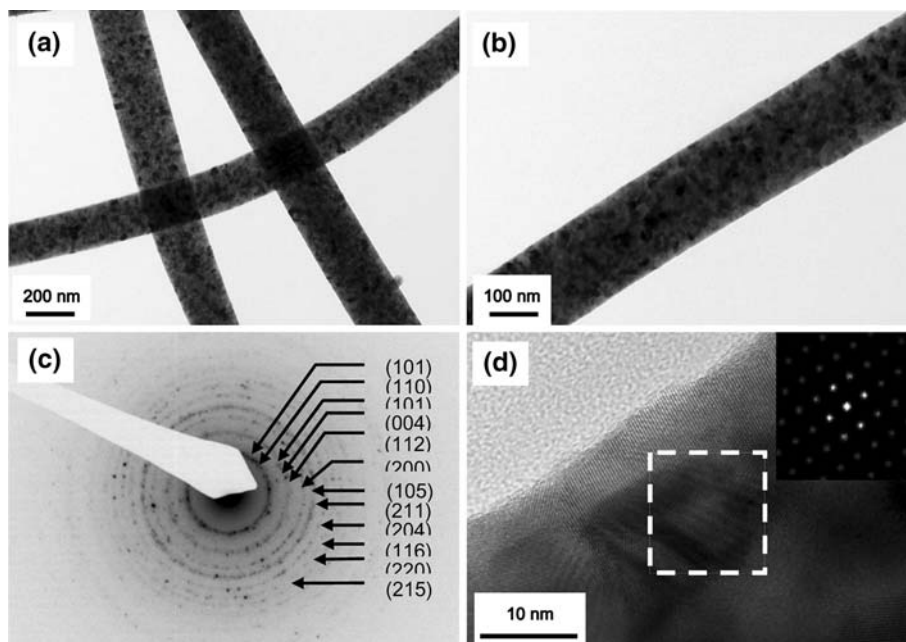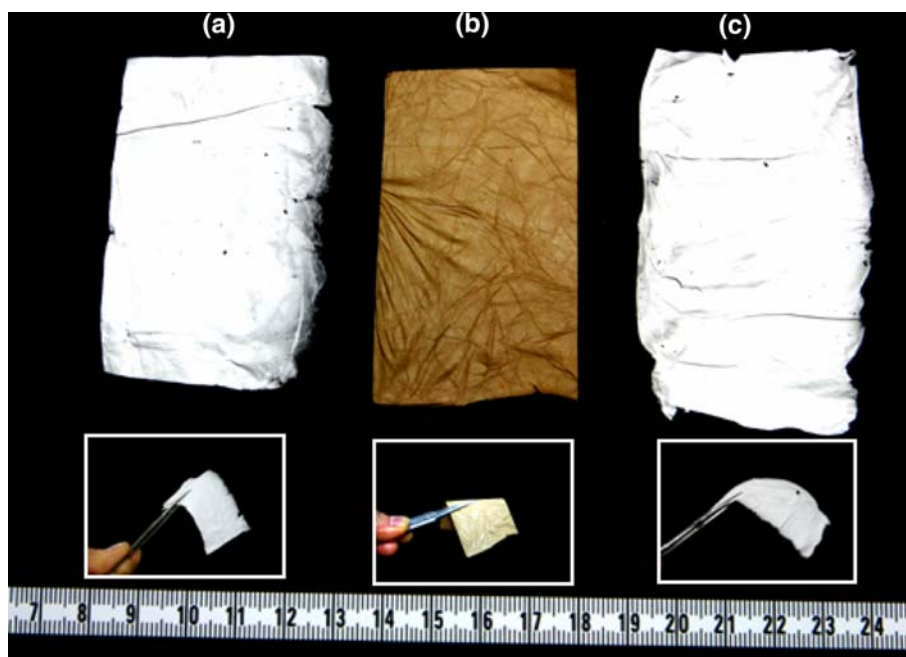

Fig. 6 Photos of polymer fiber mat (**a**), fiber mat heated to 275 °C (**b**), and fiber mat calcined at 700 °C for 2 h (**c**). The dark brown color of the mat in (**b**) is believed to be due to residual carbon compounds from the partially oxidized organic polymer and solvents in the fibers. The insert photos show the flexibility of the respective mats as they are held in the center by tweezers

Based on our best knowledge and analysis, it was speculated that the origin of flexibility of TiO_2 nanofiber mat could come from physical entanglements between TiO_2 nanofibers [8]. As shown in Fig. 1c, the lengths of nanofibers even after the calcination process are quiet long enough to form physical entanglements. Additionally, it is worth noting that a single TiO_2 nanofiber itself is quiet brittle after the calcinations process even though Young's Modulus, indicating stiffness of materials, is dramatically increased in general [21]. As shown in Fig. 1c, there are a few fused junction points between

TiO_2 nanofibers. It is believed that mechanical strengths at the partially fused junction points of TiO_2 nanofiber mats are much weaker compared with those of the main nanofibers. Therefore, during flexibility test, the main nanofibers do not break down even though the fused nanofibers are separated each other. Therefore, the partially fused junction points can increase toughness without sacrificing the flexibility of TiO_2 nanofiber mats, as shown in Fig. 7. However, more systematic studies should be needed to determine the mechanism of the high flexibility of titania fiber mats.
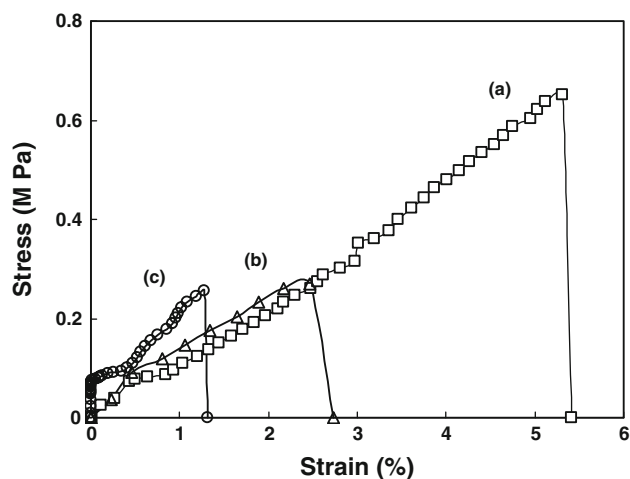
Fig. 7 Tensile stress–strain curve of composite polymer mat (*a*), fiber mat heated to 275 °C (*b*) and fiber mat calcined at 700 °C for 2 h (*c*)

To determine the mechanical strength and toughness of fiber mats, tensile tests were conducted and their stress–strain curves were constructed as shown in Fig. 7. As expected, the ultimate tensile strength (0.66 MPa) and strain at break (5.4%) of the polymer fiber mats are higher than those of heated fiber mats at 275 °C (0.25 MPa, 2.7%) and 700 °C (0.25 MPa, 1.3%). However, calcined titania nanofiber mats at 700 °C exhibit a higher Young's modulus (461 MPa) than those of the polymer fiber mats (21 MPa) and the mats heated to 275 °C. Young's modulus of the as-electrospun nanofiber increased about 20 times after the calcination at 700 °C while the strain at break of the calcinated nanofiber decreased compared with that of the as-electrospun nanofiber. This result could due to the removal of the ductile PVP polymer during the calcination process and TiO_2 inorganic crystals were formed during the calcination process [28]. The mechanical properties are summarized in Table 1. Since the titania nanofiber mats are tough with a high mechanical strength, these flexible titania nanofibers be handled without any difficulties, which can expand the range of practical applications of titania nanomaterials, such as in catalysis, membranes, and sensors.

Table 1 Mechanical properties of three different mats: unheated composite polymer fibers, fibers heated to 275 °C and fibers calcined at 700 °C

	Young's modulus (MPa)	Tensile strength (MPa)	Strain at break (%)
Unheated	21	0.66	5.4
275 °C	80	0.25	2.7
700 °C	461	0.25	1.3

4 Conclusions

Titania fibers containing both anatase and rutile crystalline structures were successfully fabricated by electrospinning and subsequent calcination at 700 °C for 2 h of the PVP polymer and titania precursor. Morphological investigation using SEM and TEM clearly indicated that the titania fibers maintain the continuous fiber forms of the polymer template. The average diameter of the fibers decreased from 500 to 180 nm after calcination. Based on the experimental results of TGA and FT-IR, the polymer and solvents are completely removed from the fibers after calcination at 700 °C for 2 h. The titania fiber mat produced in this method exhibited a significant flexibility. The tensile strength declined with calcination but the Young's modulus increased. The flexibility of the titania fiber mats provides opportunity for new applications of these materials.

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