Titanium (IV) oxide nanofibers by combined sol–gel and electrospinning techniques: preliminary report on effects of preparation conditions and secondary metal dopant

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Abstract

Sol–gel and electrospinning techniques were incorporated to produce polyvinylpyrrolidone (PVP)/titanium (IV) oxide composite nanofibers from solutions containing PVP and titanium tetraisopropoxide. Diameters of the obtained composite fibers were in the range of 120–350 nm. The effects of PVP concentration and electrostatic field strength on size and size distribution of the as-spun fibers were investigated. Calcination of these composite fibers at 500 °C resulted in pure anatase titania nanofibers without contamination of the other phases. The effects of calcination temperature and time on phase and size of the as-spun titania fibers were also investigated in this study. Moreover, the effect of silicon secondary metal dopant on morphology, crystalline phase, and thermal stability of the resulting titania fibers was also discussed.

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1. Introduction

Titanium (IV) oxide or titania (\(\text{TiO}_2\)) is one of the most common materials for a variety of applications such as catalytic devices, sensors, solar cells, and other optoelectronic devices [1,2]. Titania is a wide bandgap semiconductor with many interesting properties, such as transparency to visible light, high refractive index and low absorption coefficient. Other than these properties, it has been known to be an excellent catalyst in the field of photocatalytic decomposition of organic materials. Therefore, titania has been employed for organic pollutant treatment in the environmental applications [3]. Titania is known to have three natural polymorphs, i.e. rutile, anatase, and brookite. Only anatase is generally accepted to have significant photocatalytic activity.

Titania can be synthesized by various techniques, such as precipitation [4], chemical vapor deposition [5], hydrothermal method [6], and glycothermal method [7]. Another common technique that can result in titania with extremely high surface area is sol–gel method [8]. In this preliminary work, the sol–gel method was combined with the electrostatic spinning or electrospinning technique to produce titania nanofibers.

Electrospinning technique is a relatively simple and versatile method for fabricating ultrafine fibers with diameters ranging from tens of nanometers to submicrometers. Typically in this technique, a polymer solution or melt is ejected from a small opening or a nozzle under the influence of a strong electrostatic field. Electrostatic charges built upon the surface of a droplet induces the formation of a jet, which is subsequently stretched to form a continuous ultrathin fiber. During its flight to a collective target, the ejected, charged jet dries out, leaving ultrathin fibers on the target. The non-woven mat has a high surface area with relatively small pore size [1,2,9]. Amorphous titania nanofibers were successfully prepared by the electrospinning of a mixture of titanium isopropoxide, acetic acid, and a high molecular weight polyvinylpyrrolidone (PVP) [1].
Anatase is an unstable polymorph of titania. Phase transformation from anatase to rutile, the less chemically active polymorph, takes place at temperatures as low as 300 °C. However, the transformation temperature strongly depends upon how titania is synthesized [10]. Anatase titania that transforms to rutile at a high temperature is considered to exhibit good thermal stability. In catalytic application, large surface area and reasonably good thermal stability is often desired. Therefore, many studies have been devoted to improve the thermal stability of titania using additives such as silicon [7] and aluminum [11]. Furthermore, it has been also reported that the addition of a secondary metal dopant can enhance the photocatalytic activity of the resulting titania. Anatase/silica composite nanoparticles exhibited a much better photocatalytic activity than that of the pure anatase [8,12].

The main objectives of this study are to investigate the effects of solution, spinning, and calcination conditions on morphological appearance and crystal structure of the resulting titania fibers. The effect of the addition of silicon as the secondary metal doping on the thermal stability of the resulting titania fibers was also investigated.

2. Experimental

In a typical procedure, 1.5 g of titanium tetraisopropoxide (TIP) was mixed with 3 ml of acetic acid and 3 ml of ethanol. The solution was rest for 10 min before being added into 7.5 ml of polyvinylpyrrolidone (PVP, $M_w=1,300,000$ Da) solution in ethanol. The concentration of the PVP solution was varied between 7 and 13 wt% and the resulting mixture was constantly stirred for 10 min. Tetraethyl orthosilicate (TEOS) was finally added to the as-prepared mixture. The amount of TEOS was typically 2 wt% (unless stated otherwise) based on the total amount of the final mixture and the mixture was constantly stirred for another hour. The as-prepared solution was referred to as the spinning solution.

The spinning solution was immediately loaded into a plastic syringe. A blunt-ended 20-gauge stainless steel needle was used as the nozzle. The emitting electrode from a Gamma High Voltage Research ES30P power supply capable of generating DC voltages up to 30 kV was attached to the needle. The grounding electrode from the same power supply was attached to a piece of aluminum foil which was used as the collector plate and was placed approximately 7 cm below the tip of the needle. Upon the application of a high voltage ranging between 9 and 22.5 kV across the needle and the collective plate, a fluid jet was ejected from the nozzle. As the jet accelerated towards the collector, the solvent evaporated, leaving only ultrathin fibers on the collector. The obtained fibers were left exposed to moisture for approximately 5 h to allow complete hydrolysis of TIP and consequently subjected to calcination at a high temperature ranging between 500 and 800 °C for 3 h to remove residual PVP.

Morphology and size of the as-prepared titania fibers were observed by a JEOL JSM 5800 scanning electron microscope (SEM). Crystalline phase of the fibers was identified by a Siemens D5000 X-ray diffractometer with a Cu Kα radiation and the functional groups by a Nicolet Impact 400 Fourier-transformed infrared spectroscopy (FT-IR).

![SEM images](image-url)  
Fig. 1. SEM images of pre-calcined as-spun fibers from spinning solutions containing (a) 7 wt%, (b) 9 wt%, or (c) 13 wt% PVP solution. The applied electrostatic field strength was 9 kV/7 cm.
3. Results and discussion

3.1. Effects of spinning conditions

By applying a high electrical potential across the syringe needle and the collector plate, fibers were spun and deposited as a non-woven mat on the collector plate. SEM images of these fibers confirm that the obtained products were indeed a collection of ultrafine fibers with smooth surface.

The effects of PVP concentration of the spinning solutions on morphology of the pre-calcined as-spun fibers are shown in Fig. 1. It should be noted that the applied electrostatic field strength was fixed at 9 kV/7 cm. Clearly, ultrathin fibers with average diameter being as low as about 200 nm were produced from the spinning solution with PVP concentration of 7 wt%. Increasing PVP concentration led to an increase in the fiber diameters with broader distribution. The increase in the fiber diameters with increasing PVP concentration should be a result of the increase in the viscosity of the spinning solutions [9]. However, the increase in the viscosity of the spinning solutions could lead to non-uniform ejection of the jet, when the viscosity becomes too great.

The effect of applied electrostatic field strength on the pre-calcined fiber structure is shown in Fig. 2. It should be noted that the PVP concentration in the spinning solution was fixed at 13 wt%. Apparently, with increasing electrostatic field strength, the fibers obtained appeared to be smaller in diameter with narrower distribution. This is in contrast to what was observed on the effect of PVP concentration. Increasing electrostatic field strength resulted in an increase in both the electrostatic force, which is responsible for the transport of the charged jet to...
the collective target, and the Coulombic repulsion force, which is responsible for the stretching of an ejected jet segment [9]. The increased electrostatic force could lead an increase in the mass throughput of the material from the nozzle, while the increased Coulombic stretching force could lead to a decrease in the fiber diameters.

It is evident from Fig. 2 that the diameters of the fibers obtained appeared to be smaller with increasing electrostatic field strength. Such an observation should be due solely to the increase in the Coulombic repulsion force. Fig. 3 summarizes the relationships of the diameters of the pre-calcined fibers with respect to PVP concentration of the spinning solutions and applied electrostatic field strength. Noted that the error bars in the figure represents standard deviation of the fiber diameter data.

3.2. Properties of titania nanofibers

XRD analysis revealed that all of the as-spun fibers prior to calcination were amorphous (results not shown). Crystallization, however, took place during the calcination. The as-calcined fibers were anatase titania without contamination of the other phases. As evidently shown in Fig. 4, significant shrinkage occurred during calcination. Furthermore, the as-calcined fibers appeared to be more distorted and the surface appeared to be more rough, even though calcination did not affect much the fibrous nature of the fibers. Fig. 5 shows the relationship between the diameters of the as-calcined titania fibers and the calcination temperature in comparison with the diameters of the pre-calcined ones. Apparantly, the higher the calcination temperature, the greater the shrinkage. The shrinkage mainly resulted from the removal of organic contents, i.e. PVP matrix, from PVP/titania composite fibers during the calcination process. This was supported by the IR spectroscopic analysis (see Fig. 6) that the absorption bands in the range of 1000–2000 cm$^{-1}$, which corresponds to the bending and stretching frequencies of PVP, diminished after calcination. Instead, the band associated with the vibrational mode of O–Ti–O bonding of the anatase phase at the wave number of around 470 cm$^{-1}$ was clearly observed.
In addition, no sign of other hydrocarbon impurities was detected in the as-calcined fibers.

3.3. Effect of silicon as secondary metal dopant

Silicon was added into titania fibers by doping the spinning solution with TEOS, as previously described. The resulting fibers were calcined and analyzed. The presence of silicon in the as-calcined titania fibers was evident from the infrared absorption band at the wave number of around 1100 cm\(^{-1}\), which corresponds to the vibrational mode of O–Si–O bonding [see curve (c) in Fig. 6].

The effect of silicon doping content on the morphology of titania fibers was also observed. Fig. 7 shows SEM images of silicon-doped titania fibers (doped with either 1 or 2 wt% TEOS; the PVP concentration was 13 wt%, the spinning condition was 9 kV/7 cm, and the calcination temperature was 600 °C) in comparison with the undoped titania fibers. Interestingly, the diameters of the resulting titania fibers were significantly reduced by silicon addition. These observation was in agreement with the finding by Viswanath and Ramasamy [13] that incorporation of silicon atoms into titania lattice resulted in a smaller crystallite size.

The thermal stability of the as-prepared doped and undoped titania fibers was assessed by monitoring the crystalline phase of the fibers as a function of calcination temperatures. According to XRD patterns shown in Figs. 8 and 9, it was found that the obtained titania fibers doped with 2 wt% TEOS remained in pure anatase phase even when the calcination temperature was 600 °C, while the obtained undoped titania fibers showed an evident of the transformation into the rutile phase. At 800 °C, only rutile phase was found in the undoped titania fibers, while the silicon-doped titania ones still contained appreciable

![Fig. 7. SEM images of (a) undoped titania fibers and titania fibers doped with TEOS in various amounts: (b) 1 wt% and (c) 2 wt% after being calcined at 600 °C. The PVP concentration of the spinning solution was 13 wt% and the applied electrostatic field strength was 9 kV/7 cm.](image)

![Fig. 8. XRD pattern of undoped titania fibers calcined at various temperatures: (a) 500 °C, (b) 600 °C, and (c) 800 °C. The PVP concentration of the spinning solution was 13 wt% and the applied electrostatic field strength was 9 kV/7 cm.](image)
amount of the anatase phase. As previously mentioned, 
titania that transforms from anatase to the other phases at a 
higher calcination temperature is considered to exhibit 
better thermal stability, which is very desirable for catalytic 
applications. Consequently, addition of silicon was proved 
beneficial to increase the thermal stability of the resulting 
titania fibers.

4. Conclusion

In the present contribution, pure titanium (IV) oxide and 
silicon-doped titanium (IV) oxide nanofibers were success- 
fully prepared by combined sol–gel and electrospinning 
techniques from solutions containing polyvinylpyrrolidone 
(PVP) and titanium tetraisopropoxide after calcination at 
elevated temperatures. The average diameters of the pre-
calcined as-spun fibers were in the range of about 
120–350 nm, while those of the post-calcined ones were in 
the range of about 100–230 nm. The appearance of both 
pre-calcined and post-calcined fibers was regular, with that 
of the post-calcined fibers exhibiting rougher surface. The 
choice of the calcination temperature had a strong influence 
on the crystalline phase formation of the as-prepared titania 
fibers, with the transformation from anatase to rutile 
occurring more readily with increasing calcination 
temperature. Addition of silicon as the second metal dopant 
helped increase the thermal stability of the resulting titania 
nanofibers.

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