Fabrication of TiO_2 Nanofibers from a Mesoporous Silica Film

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TiO_2 nanofibers have been made by impregnating a mesoporous silica film with $TiCl_4$ followed by hydrolysis in air. The TiO_2 nanofiber morphology can be varied by controlling the pore size and pore volume of the mesoporous silica film. TiO_2 nanofiber diameters were in the range of 30−200 nm. The as-synthesized nanofibers are amorphous but crystallize to anatase at 250 °C without a change in morphology.

Introduction

Nanostructured TiO_2 films have attracted attention for a great variety of applications, such as dye-sensitized solar cells,[1,2] photocatalysis,[3−6] various cleaning devices,[7−9] and antifog windows.[10−12] A number of techniques have been used to make TiO_2 films, including evaporation,[13,14] sputtering,[15,16] sol−gel,[17,27] chemical vapor deposition (CVD),[18−25] plasma-enhanced chemical vapor deposition,[26] and pulsed laser deposition.[28] It is known that many of these applications would benefit from high surface to volume particles. For example, the maximum photoconversion efficiency for water splitting has been increased by more than 2-fold through replacing TiO_2 nanocrystalline films with TiO_2 nanowires.[29]

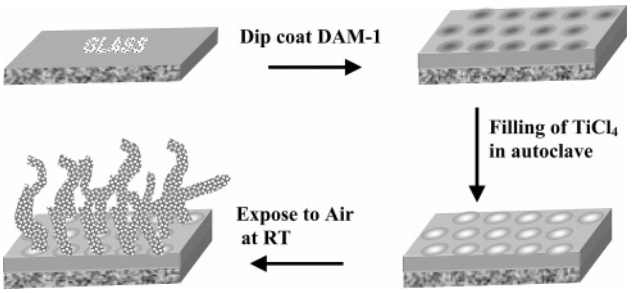

Figure 1. Scheme for the formation of TiO_2 nanofibers from mesoporous silica films.

Recently, Wu and Yu[30] synthesized TiO_2 nanorods using metal-organic chemical vapor deposition (MOCVD). Peng and Chen[31] fabricated rutile TiO_2 nanorod arrays by oxidizing titanium metal with acetone as the oxygen source. Weng et al.[32] reported the synthesis of needlelike rutile TiO_2 nanostructures on a silica substrate containing TiO_2 seeds prepared through a thin PS-*b*-P4VP diblock copolymer template. TiO_2 nanotubes and fibers have also been prepared under hydrothermal conditions[33] as well as by treatment of a dense film with H_2 at 700 °C.[34] Miao et al.[35] prepared anatase TiO_2 nanowires within the pores of an anodic aluminum oxide (AAO) template by a cathodically induced sol−gel method. In this case, formation of TiO_2 nanofibers takes place inside the pores but access to the fibers requires dissolution of the AAO template.

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(1) Nazeeruddin, M. K.; Kay, A.; Rodico, I.; Humphry-Baker, R.; Liska, P. Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
(2) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(3) Lachheb, H.; Puzenat, F.; Houas, A.; Ksibi, M.; Elaloui, F.; Guillard, C.; Herrmann, J. M. *Appl. Catal., B* **2002**, *39*, 75.
(4) Linsebrigler, A. L.; Lu, G.; Yates, J. T. *Chem. Rev.* **1995**, *95*, 735.
(5) Tanguay, J. F.; Suib, S. L.; Coughlin, R. W. *J. Catal.* **1989**, *17*, 335.
(6) Sivalingam, G.; Nagaveni, K.; Hegde, M. S.; Madras, G. *Appl. Catal. B: Environ.* **2003**, *45*, 23.
(7) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, *386*, 143.
(8) Sunada, K.; Kikuchi, Y.; Hashimoto, K.; Fujishima, A. *Environ. Sci. Technol.* **1998**, *32*, 726.
(9) Cai, R.; Kubota, Y.; Shuin, T.; Hashimoto, K.; Fujishima, A. *Canc. Res.* **1992**, *52*, 2346.
(10) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431.
(11) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M. *Adv. Mater.* **1998**, *10*, 135.
(12) Wang, R.; Sakai, N.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Phys. Chem. B* **1999**, *103*, 2188.
(13) Brown, W. D.; Grannemann, W. W. *Solid-State Electron.* **1978**, *21*, 837.
(14) Grosslaus, W.; Unshan, R. F. B. *J. Vac. Sci. Technol.* **1975**, *12*, 593.
(15) Schiller, S.; Beister, G.; Sieber, W.; Schirmer, G.; Hacker, E. *Thin Solid Film* **1981**, *83*, 239.
(16) Suhail, M. H.; Mohan Rao, G.; Mohan, S. *J. Appl. Phys.* **1992**, *71*, 1421.
(17) Yoko, T.; Yuasa, A.; Kamiya, K.; Sakka, S. *J. Electrochem. Soc.* **1991**, *138*, 2279.
(18) Yeung, K. S.; Lam, Y. W. *Thin Solid Films* **1983**, *109*, 169.
(19) Fuyuki, T.; Matsunami, H. *Jpn. J. Appl. Phys.* **1986**, *25*, 1288.
(20) Williams, L. M.; Hess, D. W. *J. Vac. Sci. Technol. A* **1983**, *1*, 1810.
(21) Chen, Z. X.; Derking, A. *J. Mater. Chem.* **1993**, *11*, 1137.
(22) Fictorie, C. P.; Evans, J. F.; Gladfelter, W. L. *J. Vac. Sci. Technol. A* **1994**, *12*, 1108.
(23) Lu, J. P.; Raj, R. *J. Mater. Res.* **1991**, *6*, 1913.
(24) Siefering, K. L.; Griffin, G. L. *J. Electrochem. Soc.* **1990**, *137*, 814.
(25) Frenck, H. J.; Wulisch, W.; Kuhr, M.; Kassing, R. *Thin Solid Films* **1991**, *201*, 327.
(26) Huang, S. S.; Chen, J. S. *J. Mater. Sci: Mater. Electron* **2002**, *13*, 77.
(27) Miki, T.; Nishizawa, K.; Suzuki, K.; Kato, K. *Mater. Lett.* **2004**, *58*, 2751.
(28) Usui, H.; Miyamoto, O.; Nomiyama, T.; Horie, Y.; Miyazaki, T. *Sol. Energy Mater. Sol. Cells* **2005**, *86*, 123.
(29) Khan, S. U. M.; Sultana, T. *Sol. Energy Mater. Sol. Cells* **2003**, *76*, 211.
(30) Wu, J. J.; Yu, C. C. *J. Phys. Chem. B* **2004**, *108*, 3377.
(31) Peng, X.; Chen, A. *J. Mater. Chem.* **2004**, *14*, 2542.
(32) Weng, C. C.; Hsu, K. F.; Wei, K. H. *Chem. Mater.* **2004**, *16*, 4080.
(33) Yuan, Z. Y.; Su, B. L. *Colloids Surf. A.* **2004**, *241*, 173.
(34) Yoo, S.; Akbar, S. A.; Sandhage, K. H. *Ceram. Int.* **2004**, *30*, 1121.
(35) Miao, Z.; Xu, D.; Ouyang, J.; Guo, G.; Zhao, X.; Tang, Y. *Nano Lett.* **2002**, *2*, 717.

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Table 1. Preparation Conditions and Physiochemical Properties of the Mesoporous Silica Films and TiO_2 Nanofibers[a]

samples	mesoporous materials	BET surface areas (m^2/g)	pore volume (cm^3/g)	pore size (Å)	wall thickness (Å)	thickness of silica layer (μm)	diameter of TiO_2 fibers (nm)
film A	b	444	0.21	26.5	24.3	0.94	50
film B	c					1.03	no fibers
film C	bare glass						no fibers
film D	d	605	0.42	37.8	28.2	1.08	200
film E	e	1075	0.53	17.0	69.2	1.34	30
film F	f	739	0.56	38.0	99.8	1.41	100

[a] For films A, B, C, and D, they were calcined at 400 °C. [b] A gel with a recipe of 0.25 g of Vit E + 35 mL of EtOH + 2.5 mL of 1 M HCl + 1 g of TEOS. [c] Without calcination after being casted the same silica gel as film A. [d] A gel with a recipe of 0.45 g of Vit E + 35 mL of EtOH + 2 mL of 1 M HCl + 1 g of TEOS. [e] A gel with a recipe of 0.2 g of P123 + 0.15 g of CTAB + 5 mL of EtOH + 1.5 mL of 4 M HCl + 1 g of TEOS. [f] A gel with a recipe of 0.35 g of P123 + 5 mL of EtOH + 1.5 mL of 2 M HCl + 1 g of TEOS.

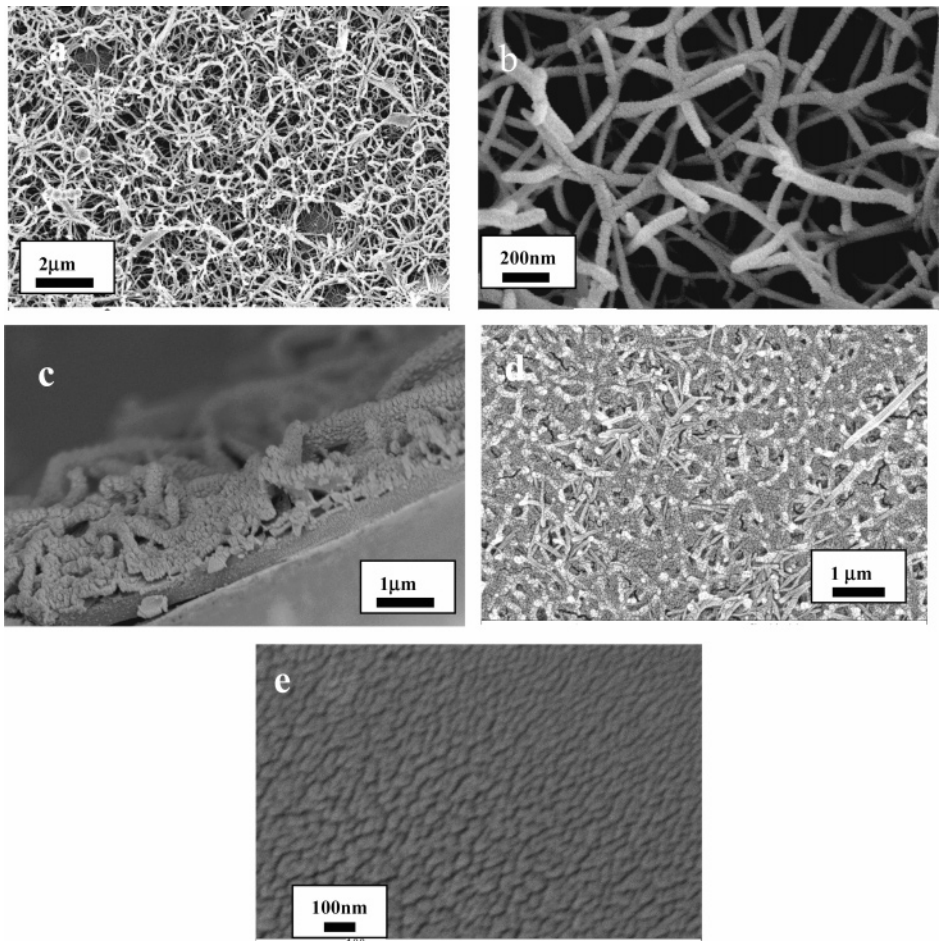

Figure 2. SEM images (a) and (b) are top views of film A, and image (c) is a cross section of film A; image (d) is film C and image (e) is film D after heating at 400 °C.

The confined channels of mesoporous silica powder or silica films have been used to prepare nanoscale metals and metal oxides.[36−41] In these studies, one common characteristic is that all the desired products formed inside the mesopores of the silica powders or films. Recovery of the nanoparticles in the pores also requires dissolution of the silica framework which could partially dissolve the encapsulated species. In the present work, a mesoporous silica film was employed as a template to grow TiO_2 nanofibers. This was accomplished by filling the mesopores with $TiCl_4$ under pressure followed by hydrolysis. The $TiCl_4$ diffuses out of the pores, making nanofibers 30−150 nm in diameter. The fibers are not formed on the bare glass substrate or on the silica film with the mesopores stuffed with organic template, which is consistent with the role of the mesopores in growing the nanofibers. Additionally, the mesopore diameter has an effect on the diameter of the TiO_2 nanofibers which is also consistent with the template role of the silica film.

(36) Omer, D.; Ivana, S.; Neil, C.; Geoffrey, A. O. *Adv. Funct. Mater.* **2003**, *13*, 30.
(37) Atsushi, F.; Hidenobu, A.; Yoko; Yusuke, A.; Masaru, I. *Nano Lett.* **2002**, *2*, 793.
(38) Shin, H. J.; Ryoo, R.; Liu, Z.; Terasaki, O. *J. Am. Chem. Soc.* **2001**, *123*, 1246.
(39) Coleman, N. R. B.; Morris, M. A.; Spalding, T. R.; Holmes, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 187.
(40) Gao, F.; Lu, Q.; Zhao, D. Y. *Adv. Mater.* **2003**, *15*, 739.
(41) Han, Y. J.; Kim, J. M.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2068.

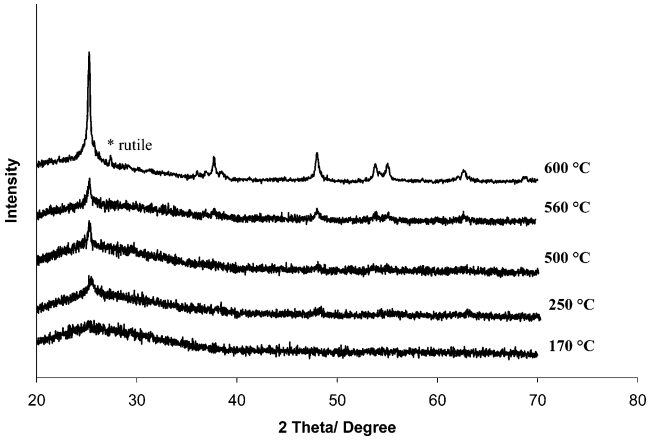

Figure 3. XRD patterns of TiO_2 nanofibers growing on film A after heating at 170, 250, 500, 560, and 600 °C.

Experimental Section

2.1. Materials. Tetraethoxysilane (TEOS, Aldrich), hydrochloric acid (Mallinckrodt), vitamin E TPGS (Eastman), ethyl alcohol (Aldrich), Pluronic P123 (BASF), cetyltrimethylammonium bromide (CTAB, Aldrich), and $TiCl_4$ (Chemat technology, Inc.) were used as received.

2.2. Preparation of Mesoporous Silica Films. The precursor for the casting sol solution is prepared from two solutions. One is a template solution, containing the template dissolved in ethanol (EtOH). The other is a silica solution, which contains a mixture of tetraethyl orthosilicate (TEOS), EtOH, distilled water, and hydrochloric acid. The specific recipes are listed in Table 1. These template and silica solutions are mixed and then condensed by partially evaporating EtOH at room temperature. The gel is then cast onto glass slides, dried at room temperature for 5 h, and calcined at 400 °C for 10 h.

2.3. Preparation of TiO_2 Nanofiber Films. Glass slides covered with the mesoporous silica film were placed in a 120 mesh stainless steel screen basket which was positioned in a 23 mL Teflon-lined autoclave 4 cm above 4 mL of $TiCl_4$. The filling of $TiCl_4$ in mesopores was conducted by heating the autoclave at 90 °C for 24 h under autogenous pressure. The films were then removed from the autoclave and hydrolyzed in air for 10 min at room temperature with 50% humidity and then dried at 90 °C followed by calcination at 400 °C. For comparison, the same experiment was conducted on the glass slides coated with mesoporous silica but without removal of the organic template. The experiment was also conducted on bare glass slides.

2.4. Characterization. The crystallinity of the TiO_2 nanofibers was determined by powder X-ray diffraction (XRD) (Scintag XDS 2000 X-ray diffractometer with Cu Kα radiation). The fiber morphology was evaluated by scanning electron microscopy (LEO 1530 VP field emission SEM) from Au/Pd coated samples. Surface area and pore size were measured using a Quantachrome Autosorb I, from N_2 absorption and BJH analysis.

Results and Discussion

Four mesoporous silica films to be used as templates were made using Vitamin E TPGS and P123 as well as P123 and CTAB as listed in Table 1. The XRD patterns of these films (not shown) revealed ordered mesoporous structures. The pore sizes of these silica films are also listed in Table 1. To make TiO_2 nanofibers, the mesoporous silica films were subjected to $TiCl_4$ vapor in an autoclave at 90 °C for 24 h, and then exposed to air for hydrolysis, as illustrated in Figure 1. It was thought that TiO_2 might form in the pores but surprisingly the volatile $TiCl_4$ vaporizes from pores and reacts with moisture outside the pores of the silica film; thus, TiO_2 nanofibers form on the silica surface.

For the sample film A, Vitamin E TPGS was used as the template to create a 0.94 μm thick DAM-1[42] film with mesopores 2.65 nm in diameter. Upon filling the sample film with $TiCl_4$ and after hydrolysis in air, Figure 2a shows a film composed of TiO_2 nanofibers covering the surface of the silica film. The TiO_2 nanofibers have a diameter of $\sim$50 nm as displayed in the SEM image in Figure 2b. The TiO_2 nanofibers are larger than the mesopores after complete hydrolysis. It is speculated that the $TiCl_4$ begins to diffuse out of the pores and begins to hydrolyze, nucleating TiO_2 at the pore opening and/or surface space between pores. The escaping $TiCl_4$ feeds the growing fiber and eventually more than one fiber merges to form the 50 nm size fibers. The XRD patterns in Figure 3 indicate that as-made TiO_2 nanofibers are amorphous. However, with heating the anatase phase begins to form as low as 250 °C, and the particle size is $\sim$50 nm as calculated from the XRD pattern using the Scherrer equation. The anatase phase begins to convert to rutile at 600 °C; meanwhile, the particle size increased to $\sim$58 nm.

As a control experiment (film B), a mesoporous silica film containing the Vitamin E TPGS template was treated with $TiCl_4$ in the same way as film A, but after exposure to air, a film with what appears to be embedded TiO_2 nanorods were observed on the surface (Figure 2d). With the mesopores partially filled with Vitamin E TPGS, the $TiCl_4$ should mainly adsorb on the outer surface and defect sites. Meanwhile, there are no TiO_2 fibers grown on the bare glass slides (Figure 2e), which further demonstrates the importance of the mesopores for formation of TiO_2 nanofibers on the silica films.

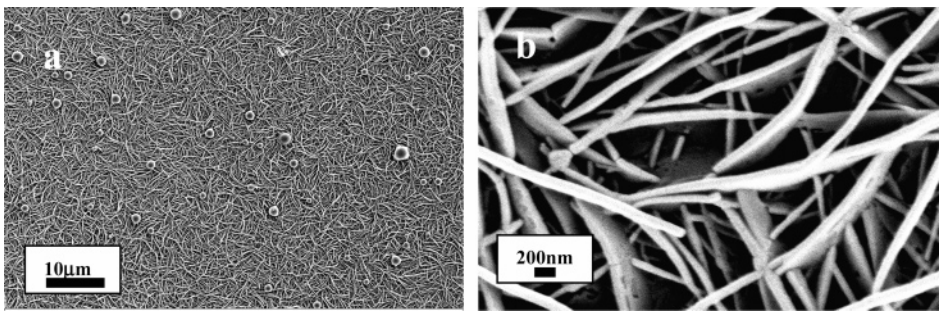

Figure 4. SEM images of film B after heating at 400 °C.

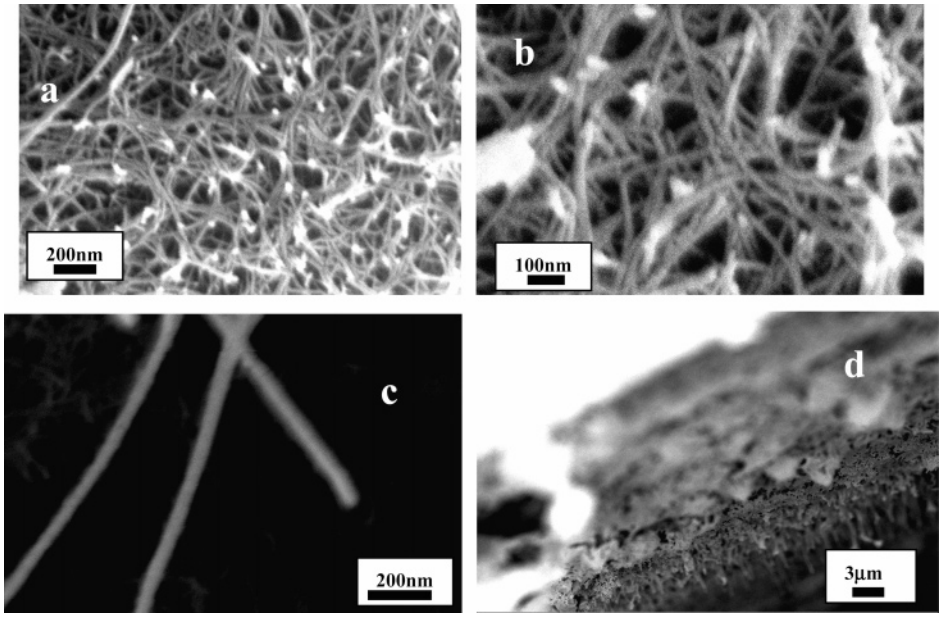

Figure 5. SEM images of film E after heating at 400 °C, where images (a)−(c) are top views and image (d) is a cross section.

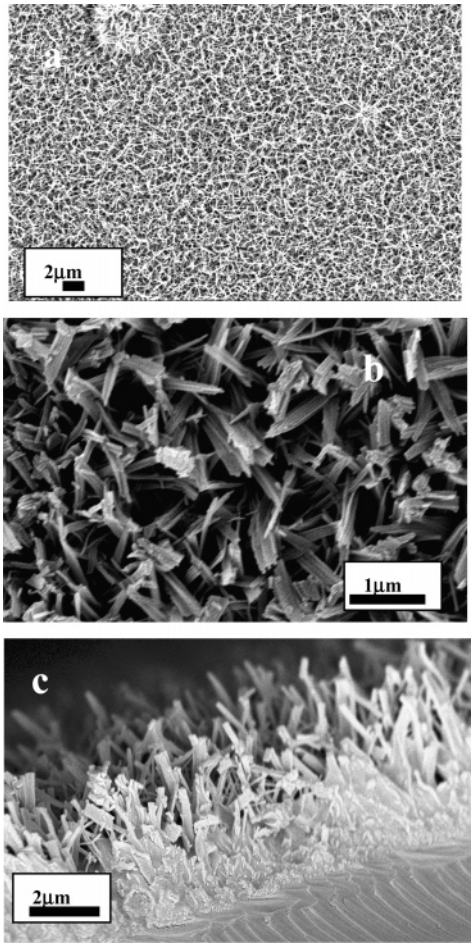

Figure 6. SEM images of film F after heating at 400 °C, where images (a) and (b) are top views and image (c) is a cross section.

When the amount of Vitamin E TPGS was changed in the DAM-1 recipe, film D was prepared with bigger pores (3.78 nm) and pore volume (0.42 cm^3/g) in the silica film. Additionally, the mesoporous film is more ordered than film A (50 nm). After impregnation with $TiCl_4$ and after hydrolysis, the resulting TiO_2 morphology was ribbon-like as shown in Figure 4. The TiO_2 ribbons formed on the surface of the silica film, with a diameter of 200 nm, which is much bigger than those grown on film A. The increased diameter of TiO_2 may be a result of the bigger pore size in film D; in addition, the bigger pore volume may allow more $TiCl_4$ to be filled into the film, which may lead to thicker TiO_2 fibers.

To further investigate the effects of pore size and pore volume on the formation of TiO_2 nanofibers, a mesoporous silica film E with a pore size of 1.7 nm was created by using P123 and CTAB as co-templates. For film E, uniform TiO_2 nanofibers exhibited a diameter of ∼30 nm as shown in Figure 5c. When P123 was used by itself to prepare film F, the pore size and pore volume of the silica film were increased to 3.8 nm and 0.56 cm^3/g, respectively (as seen in Table 1), which is less than usual, because the pore size changes with reaction temperature and time.[43] In this case, the mesoporous silica film was made at room temperature, and the reaction time of the precursor before making the silica film was about 3 h. On the surface of film F, larger TiO_2 nanofibers were produced and the diameter was ∼100 nm which is consistent with the bigger pore size and the bigger pore volume. The SEM image in Figure 6b suggests the TiO_2 nanofibers are composed of many nanofibers fused together.

Conclusion

A novel mesh of TiO_2 nanofibers has been prepared by filling a mesoporous silica film with $TiCl_4$ at 90 °C, followed by hydrolysis in air. The size and morphologies of nanofibers appear to change with the pore size and pore volume of the silica layer. XRD patterns of the TiO_2 films indicate the TiO_2 is largely amorphous as made but crystallizes to anatase above 250 °C.

(42) Coutinho, D.; Balkus, K. J., Jr. *Microporous Mesoporous Mater*. **2002**, *54*, 229.

(43) Zhao, D. Y.; Feng, J. L.; Huo, Q.; Melosh, N.; Frederickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

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Supporting Information Available: XRD patterns of mesoporous silica films. This material is available free of charge via the Internet at http://pubs.acs.org.

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