Preparation of Mesoporous Titania Thin Films with Remarkably High Thermal Stability

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Many researchers are currently focusing on producing high surface area crystalline mesoporous titania[1] because of its applications in photocatalysis, as highly specific chemical sensors, in optoelectronic devices, in photovoltaics, and as fuel cells.[2] For many of these applications, processing the titania material as a highly thermally stable coating, or thin film, is essential. For example, the solid electrodes in fuel cells need to be stable under high operating temperature between 600 and 1000 °C.[3] However, typically with mesoporous TiO_2, the thermal treatment employed to transform the titania walls from amorphous to crystalline usually leads to a total collapse of the mesoporous network.[4] In an attempt to increase the thermal stability of mesoporous titania materials, several postsynthesis calcination methods have been developed.[5] In particular, Cassiers et al.[5a] reported that the post-treatment of uncalcined mesoporous titania powder with ammonia resulted in the formation of mesoporous crystalline titania with thermal stability up to 600 °C. Sanchez and co-workers[5b] claimed that the mesoporous anatase network could be retained with a porosity of 35% above 650 °C by applying a specific postsynthesis delayed rapid crystallization (DRC) treatment. However, calcination at 730 °C for approximately 20 min resulted in the destruction of the mesostructure. In this communication, we report the preparation of high-quality titania thin films using nonionic surfactant as the structural directing agent. The starting sol was spin-coated onto silicon wafers, and glass slides, followed by evaporation-induced self-assembly to make high-quality crack-free thin films. The thermal stability of these crystalline films can be enhanced, up to 850 °C, by post-treatment of the film in supercritical carbon dioxide (sc-CO_2)
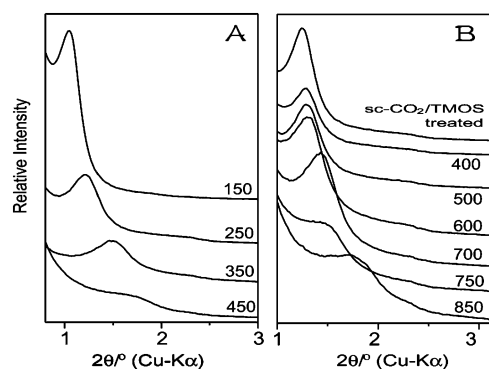

Figure 1. XRD patterns of (A) untreated and (B) sc-CO_2/TMOS-treated mesoporous titania thin films calcined at various temperatures for a duration of 1 h each.

with the presence of a small amount of precursor, such as tetramethoxysilane (TMOS).

The mesoporous titania films were prepared by spin-coating from a precursor solution prepared using titanium tetra-isopropoxide (Ti(i-PrO)$_4$, TTIP), Pluronic P104 (BASF, EO$_{18}$PO$_{58}$EO$_{18}$), HCl, and absolute ethanol with a molar ratio of 1.0:0.02:2.0:35.2 TTIP:P104:HCl:EtOH. Detailed synthesis and post-treatment procedures of titania films are provided as Supporting Information. Figure 1a shows X-ray diffraction (XRD) patterns from a mesoporous titania thin film deposited on a silicon wafer and calcined at various temperatures without CO_2 treatment. The aging and step-by-step thermal treatments allow the progressive condensation of the titania hybrid network. As observed in Figure 1a, a mesoporous nanocrystalline titania thin film is obtained with a thermal stability up to 350 °C without CO_2 treatment. The remarkable decrease in both the intensity of the (110) diffraction peaks and the (110) d-spacings with increasing calcination temperature implies contraction and shrinkage of the mesopores, and the elimination of volatile species and the surfactant template, during the process of thermal treatment. The degradation of the mesostructure is also related to the formation of nanocrystalline anatase in the inorganic wall. The d(110) spacing decreases from 8.2 to 5.9 nm after calcination at 350 °C, which corresponds to a 28% structural contraction. Calcination of the film at 450 °C results in almost total collapse of the ordered mesoporous structure.

The XRD patterns of the uncalcined mesoporous tatania thin films post-treated in sc-CO_2, with the addition of a small amount of TMOS, calcined at various temperatures are shown in Figure 1b. Unlike the untreated mesoporous films there was no significant change in the position of the (110) diffraction peak up to a temperature of 600 °C. The negligible shift of the (110) diffraction peak indicates that the ordered mesoporous structure was preserved, without contraction, during the high-temperature condensation and crystallization process. Furthermore, the width of the (110) diffraction peak did not change significantly at calcination temperatures up to 700 °C, indicating the high thermal stability of the mesoporous structure after the sc-CO_2 treatment. Calcination of the films at 850 °C for 1 h did however lead to a reduction of the d(110) spacing from 8.2 to 5.0 nm and hence a

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(1) (a) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, *396*, 152. (b) Antonelli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2014. (c) Crepaldi, E. L.; Soler-Illia, G. J. de A. A.; Grosso, D.; Sanchez, C. *New J. Chem.* **2003**, *27*, 9. (d) Bosc, F.; Ayral, A.; Albouy, P.; Guizard, C. *Chem. Mater.* **2003**, *15*, 2463.
(2) (a) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802. (b) Imhof, A.; Pine, D. J. *Nature* **1997**, *389*, 948. (c) Fujii, H.; Ohtaki, M.; Eguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 6832.
(3) He, X.; Antonelli, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 214.
(4) (a) Sayari, A.; Liu, P. *Microporous Mater.* **1997**, *12*, 149. (b) Schüth, F. *Chem. Mater.* **2001**, *13*, 3184.
(5) (a) Cassiers, K.; Linssen, T.; Meynen, V.; Voort, P. Van Der; Cool, P.; Vansant, E. F. *Chem. Commun.* **2003**, 1178. (b) Grosso, D.; Soler-Illia, G. J. de A. A.; Crepaldi, E. L.; Cagnol, F.; Sinturel, C.; Bourgeois, A.; Brunet-Bruneau, A.; Amenitsch, H.; Albouy, P. A.; Sanchez, C. *Chem. Mater.* **2003**, *15*, 4562.
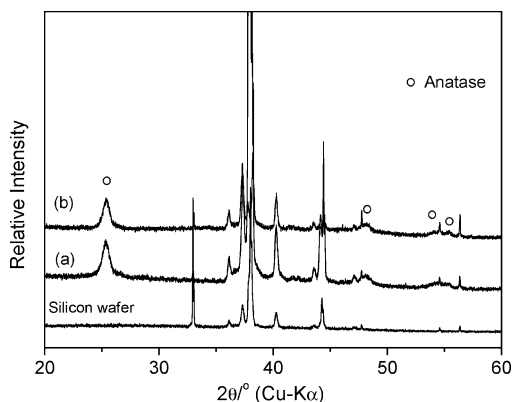
Figure 2. High-angle XRD patterns of sc-CO_2/TMOS-treated films calcined at (a) 550 °C and (b) 750 °C, respectively. That of silicon wafer calcined at 650 °C is provided for comparison.

contraction of approximately 39%. Calcination of the thin films for significant time periods at temperatures over 950 °C did lead to the deterioration of the mesostructure.

The high-angle XRD patterns of the mesoporous titania films are presented in Figure 2. The obvious appearance of the broadened $d(101)$ diffraction located at 25.4° (2θ) after the calcination, characteristic for anatase, suggests the mesostructure wall of the thin films are composed of nanosized anatase crystallites. The full width at half-maximum (fwhm) of the $d(101)$ diffraction is about 0.78 after calcination at 550 °C and reduces to 0.74 when calcined at 750 °C. The slight shift in the fwhm of the $d(101)$ peak suggests the sc-CO_2/TMOS treatment retards the crystal growth of anatase significantly. Without sc-CO_2/TMOS treatment, the growth rate of anatase is often rapid and consequently leads to the collapse of the mesostructure even at a temperature below 450 °C. It is therefore this control of the crystal growth rate which is responsible for the high thermal stability of the mesostructured thin films.

The transmission electron microscopic (TEM) images (Figure 3a) reveal that the mesopores of the sc-CO_2/TMOS treated titania films are packed in an ordered cubic arrangement even after high-temperature calcination. Upon the sc-CO_2/TMOS treatment, we do not observe unidirectional shrinkage of the cross-sectional pore structure even at calcination temperatures above 750 °C. This result is unlike previously reported mesostructured thin film deposited on other substrates[1c,6] and suggests that, after the treatment, the

walls of the thin films are strong enough to withstand the high-temperature calcinations and resist anisotropic contraction.

Further information on the microstructure of the thin films is provided by HRTEM investigations as shown in Figure 3b. It can be observed that the 750 °C calcined films are totally composed of high-crystalline anatase nanoparticles, which is in good agreement with the high-angle XRD studies. The mesopores are observed as white areas in the images. The sizes of both the nanoparticle and the mesopores are in the range of 5−8 nm. The anatase nanoparticles are randomly embedded in the mesoporous walls of the thin films. Usually, the anisotropic crystallization and growth of crystalline particles are apt to exceed the geometry of the inorganic framework and will lead to the obvious distortion or deterioration of the ordered mesopore structures.[6,7] In our samples, the randomly oriented anatase nanoparticles occupy the limited space within the channel walls, resulting in a fully crystallized ordered structure. This may be the reason the sc-CO_2/TMOS treated films exhibit such high thermal stability.

The enhanced thermal stability of the titania films therefore probably results from cooperation among sc-CO_2, TMOS, and the titania precursor. In particular, treatment with sc-CO_2 plays an important role in enhancing the thermal stability of the mesoporous titania films. In the absence of CO_2, or when the fluid pressure is less than 20.7 MPa, collapse of the ordered mesostructure occurs at temperatures above 350 °C. In addition, treatment of the titania films with TMOS vapor only in a closed vessel, as proposed by Nishiyama et al.[8] for mesoporous silica thin films, does not enhance the structural stability of the titania films significantly. A small amount of TMOS during the sc-CO_2 treatment is however essential for producing thermally stabile mesostructured films. Although there is an increase in the thermal stability of CO_2-treated films without the presence of TMOS, calcination above 550 °C leads to the complete collapse of the ordered mesostructure. We therefore ascribe the high thermal stability of the treated films to the dispersion of Si and its interactions with the titania matrix as described by O'Neil in the post-treatment of MCM-41 in supercritical fluids with aluminum isopropoxide.[9] Prior to calcination the walls of the fresh titania film are composed of small Ti-oxo-hydroxo
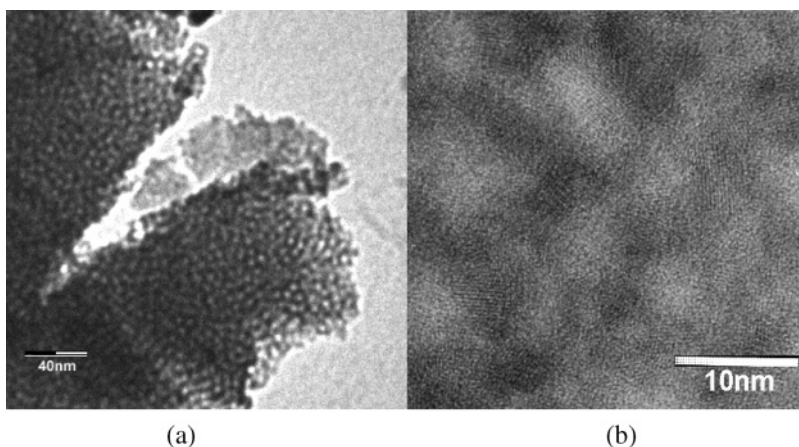

(a)	(b)

Figure 3. TEM (a) and HRTEM images (b) of the sc-CO_2/TMOS-treated titania films after calcination at 750 °C.

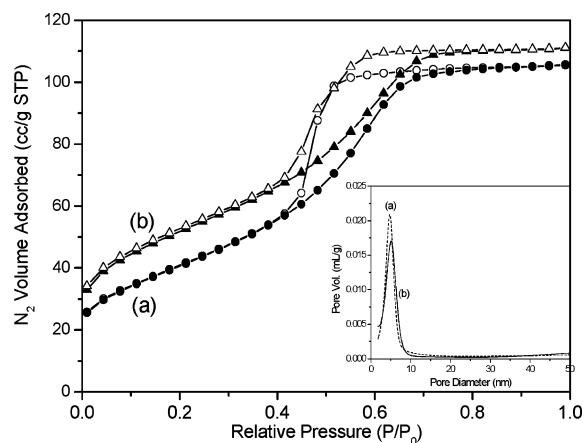Communications

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Figure 4. Nitrogen adsorption−desorption isotherm plots and pore size distribution curve (inset) for (a) untreated TiO_2 film calcined at 350 °C and (b) films treated by sc-CO_2/TMOS and then calcined at 380 °C.

Table 1. Textural Properties of (a) TiO_2 Film Treated at 350 °C and (b) Films Treated by sc-CO_2/TMOS and Then Calcined at 380 °C

sample	$d_{spacing}$ (nm)	A_{BET} (m^2/g)	V_{BJH} (mL/g)	D_{BJH} (nm)
a	5.8	147.6	0.16	4.9
b	6.9	182.9	0.16	5.1

oligomers, with some Cl atoms linked to titanium.[10] The condensation of the Ti-oxo-hydroxo oligomers and Ti−Cl groups to form high μ-oxo connectivity will contribute to the crystallographic reorganization from amorphous titania to anatase. Consequently, the growth of anatase crystal domains will deteriorate the ordered mesoporous structure. During the sc-CO_2/TMOS treatment, the Si species can penetrate the walls of the titania films and occupy both surface and near-surface sites, due to the high penetrating power of sc-CO_2 under high pressure.[11] The content of Si species in the thin film is neglectable as suggested by the XRF examination (see Supporting Information). Thus, the interactions of Si species with Ti-oxo-hydroxo oligomers does not impact the formation of nanosized anatase in the mesoporous wall but instead retards the growth of the crystalline grains when the film is calcined at a relatively high temperature. Consequently, the mesoporous titania thin films with a nanosized anatase wall are obtained, which can resist further structural contraction. Thus, the densified titania wall of the post-treated film exhibits high thermal stability with no significant contraction of the pores during the high-temperature treatment.

Nitrogen adsorption−desorption isotherms were collected at 77 K for films scratched from the substrate using Micromeritics Gemini 2375 volumetric analyzer. Figure 4 shows the N_2 adsorption−desorption isotherms of an untreated TiO_2 film at 350 °C and a film treated with sc-CO_2 and TMOS and then subsequently calcined at 380 °C. All the films examined exhibited a Type IV adsorption isotherm

with a H2 hysteresis loop. Usually, the H2 type hysteresis loop is attributed to the presence of cage-like structures associated with effects such as large pores connected by smaller openings (ink-bottle effect).[12] BJH adsorption pore distribution analysis of treated and untreated titania films calcined at 350 °C are shown in Figure 4 (inset). The narrow Gaussian pore size distribution curves imply that the materials have very regular pore channels in the mesoporous region even after the sc-CO_2/TMOS treatment. The slight increase of BJH pore size in the treated films might suggest that the small amount of TMOS used in the sc-CO_2 treatment does not condense greatly on the inner surface of the wall to block the mesopore channels. This hypothesis is supported by the increase of the BET surface area of the mesoporous titania film after sc-CO_2 treatment (Table 1). Although the mesopores are filled with surfactant, Si species can still be effectively dispersed on the inner wall surface of the mesopores due to the low interfacial tension of supercritical CO_2.[11] In our laboratory, we previously observed that sc-CO_2 can lead to the expansion of pores within mesoporous silicas.[13] Hence, it is likely that sc-CO_2 also leads to pore swelling within the titania films. This swelling effect subsequently overwhelms any shrinkage of the pores resulting from the dispersion of Si species on the inner wall surface. Swelling of the mesopores probably also accounts for the increase in the surface area and pore size distribution of the titania films after sc-CO_2/TMOS treatment.

In summary, we have developed an easy and reproducible method for preparing well-ordered and exceptionally thermally stable mesoporous titania films prepared on silicon wafers or glass slides. The sc-CO_2/TMOS treatment described allows the preparation of highly porous titania films with long-term thermal stability up to 850 °C. The work reported here has implications for the use of mesoporous TiO_2 films for applications such as photocatalyst, sensors, and energy conversion. The applications of this thermally stable thin film are underway.

Supporting Information Available: Detailed synthesis and post-treatment condition and XRF characterization (PDF). These material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Choi, S.; Mamak, M.; Coombs, N.; Chopra, N.; Ozin, G. A. *Adv. Funct. Mater.* **2004**, *14*, 335.
(7) Grosso, D.; Soler-Illia, G. J. de A. A.; Babonneau, F.; Sanchez, C.; Albouy, P.; Brunet-Bruneau, A.; Balkenende, A. R. *Adv. Mater.* **2001**, *13*, 1085.
(8) Nishiyama, N.; Tanaka, S.; Egashira, Y.; Oku, Y.; Ueyama, K. *Chem. Mater.* **2002**, *14*, 4229.
(9) O'Neil, A. S.; Mokaya, R.; Poliakoff, M. *J. Am. Chem. Soc.* **2002**, *124*, 10636.
(10) Crepaldi, E. L.; Soler-Illia, G. J. de A. A.; Grosso, D.; Cagnol, F.; Ribot, F.; Sanchez, C. *J. Am. Chem. Soc.* **2003**, *125*, 9770.
(11) (a) Johnston, K. P.; Shah, P. S. *Science* **2004**, *303*, 482. (b) Pai, R. A.; Humayun, R.; Schulberg, M. T.; Sengupta, A.; Sun, J. N.; Watkins, J. J. *Science* **2004**, *303*, 507.

(12) Krub, M.; Jaroniec, M. *Chem. Mater.* **2001**, *13*, 3169.
(13) Hanrahan, J. P.; Copley, M. P.; Ryan, K. M.; Spalding, T. R.; Morris, M. A.; Holmes, J. D. *Chem. Mater.* **2004**, 16, 424.