CHEMCOMM
Communication
www.rsc.org/chemcomm

Nanoparticle routes to mesoporous titania thin films

Young Kyu Hwang,[a] Kyoung-Chul Lee[b] and Young-Uk Kwon*[a]

[a] *Department of Chemistry and BK-21 School of Molecular Science, Sungkyunkwan University, Suwon 440-746, Korea. E-mail: ywkwon@chem.skku.ac.kr*
[b] *Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*

Received (in Cambridge, UK) 30th May 2001, Accepted 26th July 2001
First published as an Advance Article on the web 15th August 2001

Controlled aging of TiO_2 nanoparticles blended with diblock copolymers and processed into dip-coated thin films led to ordered mesostructures with cubic and hexagonal symmetries that can be transformed into mesoporous TiO_2 by calcination.

There has been much interest in porous titania for its potential applications in areas such as photocatalysis,[1] photovoltaics,[2] and proton conducting membranes.[3] However, attempted syntheses of mesoporous titania so far have achieved only limited success.[4] On the other hand, many of the possible applications of mesoporous titania require thin films with accessible pores from the film surfaces, which is not possible with the common 2D hexagonal phases that form channels parallel to the film surfaces; a bicontinuous cubic phase would be desirable. Recently, Yang *et al.* have developed a generalized method to synthesize mesoporous oxides of many non-silicon metals utilizing non-hydrolytic condensation reactions of metal halides with alcohols and Pluronic block copolymers as the structure directing agents.[5] They have synthesized mesoporous titania with a cubic structure as well as 2D hexagonal structure. However, this seemingly simple method actually involves many different reactions occurring simultaneously including condensation of metal ions and self-assembly of the block copolymer templates that are sensitively affected by the reaction conditions. Slight variations of the reaction environments often produce totally different results making this method not highly reproducible. We have sought solutions for this problem by utilizing pre-synthesized nanoparticles instead of inducing the condensation of metal halides in the presence of surfactant molecules to alleviate the system's sensitivity, and thus to make the method simpler and more reproducible. In this paper, we report our results on the synthesis of mesoporous titania films using TiO_2 nanoparticles.

The synthesis of mesoporous titania is achieved in four steps of (1) synthesis of nanoparticles, (2) blending nanoparticles with template molecules into thin films, (3) aging the blended mixtures into mesostructures under appropriate conditions, and (4) calcination to remove the organic templates. Stock solutions of TiO_2 nanoparticles were prepared according to the literature procedure with slight modifications:[6] Titanium chloride, $TiCl_4$, was dissolved in absolute ethanol to a final $TiCl_4$ concentration of 20 wt%. A mixed solution of conc. HCl and 35% H_2O_2 in a 4/1 ratio (v/v) was added and the solution was refluxed at 80 °C for 2 h. The nanoparticles so obtained have anatase structure according to electron diffraction and transmission electron microscopy (TEM, JEOL-3011, 300 keV) studies† with sizes of *ca.* 1.6–2.0 nm based on the absorption edge of 305–325 nm from UV–VIS spectroscopic data.[7] A Brij-type diblock copolymer, $C_nH_{2n+1}(OCH_2CH_2)_yOH$ (C_nEO_y) with n/y = 16/20, 16/10, or 12/4, was dissolved in the TiO_2 stock solution and stirred for 10 h at room temperature. The molar composition of the final solution was $TiCl_4/C_nEO_y/HCl/H_2O_2/EtOH/H_2O$ = 1/0.083/3.8/0.97/6.1/15. The solution was dip-coated on silicon substrates at a pulling rate of 6 cm m^{-1}. The films were dried/aged either at 10 °C for 8 d or at 18 °C for 7 d under a controlled humidity of 80%. The progress of mesostructure formation of the materials in the as-synthesized films was monitored by powder X-ray diffraction (XRD, Rigaku D/max-RC). After the film materials ordered into cubic or hexagonal mesostructures (according to XRD), the films were calcined at 450 °C for 5 h in air. The as-synthesized films had some chlorine impurity (Cl/Ti = 0.3 by EDX/TEM), which was completely removed by calcination. The film thickness was typically about 300 nm for the as-synthesized and about 100 nm for the calcined films by SEM (JEOL-35 CF) and ellipsometry (Woollam VASE instrument). The crack-free, uniform and transparent (to the naked eye) TiO_2 mesoporous thin films so obtained were characterized by XRD and TEM.

The as-synthesized film prepared with $C_{16}EO_{20}$ block copolymer formed a mesostructure after aging at 10 °C for 7 d as evidenced by the XRD peak with d = 5.8 nm [Fig. 1(a)]. The XRD patterns were featureless up to 6 d of aging, indicating the sluggish nature of the self-assembly kinetics of the film materials. The XRD peak was shifted to d = 4.1 nm upon calcination indicating a lattice contraction by about 30% [Fig. 1(b)]. Although the XRD patterns do not reveal the details of the structure with only one peak present, the TEM image of the calcined material, in Fig. 1(c), can be explained by a pseudo-cubic structure with the [100] axis parallel to the viewing direction. The repeating distance of 4.3 nm of this image is in accord with the d-value from the XRD pattern. With the limited information available from these data, we cannot determine the structure of this material. However, the coinciding d-values from the XRD and TEM data suggest that the material has a primitive cubic unit cell. The one-peak nature in the XRD

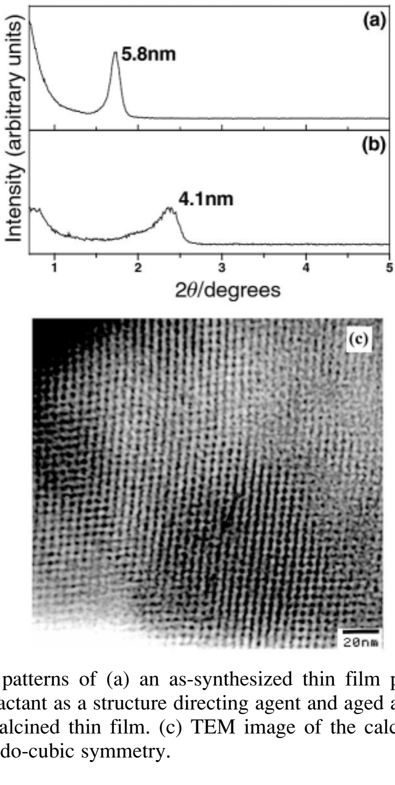

Fig. 1 XRD patterns of (a) an as-synthesized thin film prepared using $C_{16}EO_{20}$ surfactant as a structure directing agent and aged at 10°C for 7 d and (b) the calcined thin film. (c) TEM image of the calcined thin film showing pseudo-cubic symmetry.

DOI: 10.1039/b104699n

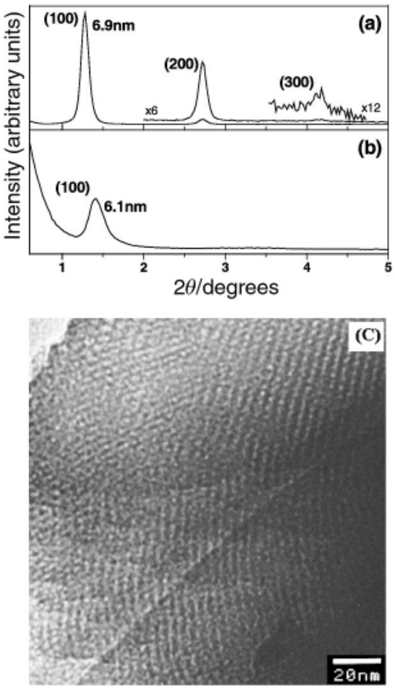

Fig. 2 XRD patterns of (a) an as-synthesized thin film prepared using using $C_{16}EO_{10}$ surfactant as the structure directing agent and aged at 18 °C for 4 d and (b) the calcined thin film. (c) TEM image of the calcined thin film that shows a 2D hexagonal structure preferentially oriented with the [100] axis parallel to the viewing direction.

pattern and the off-perpendicular axes in the TEM images suggest that the material is distorted from the ideal cubic structure, probably because the ordering of the materials is not perfect. The anisotropic lattice contraction during the calcination may also be responsible for the distorted mesostructure in the TEM image. Reflectance UV–VIS spectroscopic data on a calcined thin film shows an absorption edge of 360 nm that corresponds to a size of 3.0 nm for the anatase nanoparticles. This value agrees with the wall thickness measured from the TEM images and implies that the particle size is increased upon calcination. We have attempted to obtain better ordering of the materials by aging for longer periods of time up to 14 d, but the XRD patterns did not reveal any further peaks. Notwithstanding, it is clear that thin films of mesoporous titania with accessible pores from the film surfaces can be obtained by this procedure.

If the as-synthesized film was aged at 18 °C for 4 d instead of 10 °C for 7 d and calcined, the XRD pattern did not show any peak, indicating that a lamellar structure was not obtained. However, when $C_{16}EO_{10}$ was used instead of $C_{16}EO_{20}$ and aged at 18 °C, an XRD pattern with high order peaks that could be indexed with a 2D hexagonal or a lamellar mesostructure was obtained [Fig. 2(a)]. The XRD pattern was maintained after calcination with peaks shifted to higher angles [Fig. 2(b)] indicating a 2D hexagonal phase. The lattice parameters were a = 6.9 and 6.1 nm before and after calcination. The TEM image of the calcined sample also confirmed the hexagonal structure with channels with a repeating distance of 3.7 nm in agreement with the expected value of 3.5 nm (= $a/2$) based on the lattice parameter from XRD measurements.

Unfortunately, our TEM and XRD data did not provide any evidence of crystalline TiO_2 in the mesoporous films, probably because the particles were not well crystallized or were too small in size. Attempts to improve the crystallinity of the wall TiO_2 by calcining at higher temperatures than 450 °C caused collapse of the mesostructures, although anatase peaks were observed in the XRD patterns.

Because of the limited amount of samples available from thin films, we were not able to perform any other characterization studies such as surface area measurements. However, with the XRD and TEM data provided, it is clear that the materials we have obtained are mesoporous TiO_2.

The present system requires optimization of the reaction conditions. When different templates such as $C_{16}EO_{10}$ or $C_{12}EO_4$ were used instead of $C_{16}EO_{20}$ and aged at 10 °C, lamellar or disordered mesostructures were formed. Synthesis using $C_{12}EO_4$ and aging at 18 °C produced a lamellar structure whose lattice collapsed upon calcination. Thin films from solutions with different molar ratio of $TiCl_4/C_nEO_y$ from those given above formed poorly ordered mesostructures. However, the synthesis results are reproducible once the conditions including the composition, aging temperature and atmosphere are controlled as described. The nanoparticles in the solutions, with or without surfactant molecules, are very stable so that thin films prepared from solutions stored for up to 2 weeks under ambient conditions produce the same results.

Even after the mesostructures were formed by aging, the film materials are washed out when immersed in alcohols, indicating that the nanoparticles are not condensed into a 3D framework structure by aging alone. This observation and the strong dependency of the final mesostructure to the aging temperature resemble those of liquid crystals. Therefore, the mesostructures in the as-synthesized films can be explained by the self-assembly of the block copolymer and TiO_2 nanoparticles which, together, behave as a liquid crystal.

The method used in this paper has many advantages over those reported in the literature. First, by using block copolymers with large molecular weight and nanoparticles, the resulting mesostructures have large pores and thick walls, which can be of benefit for the utilization of semiconducting properties of transition metal oxides. Second, the results in this paper are highly reproducible as long as the conditions described are met since the complex condensation reactions of the inorganic precursors were eliminated. Third, the principles used in this work are simple and can be easily adapted to other metal oxide systems. Fourth, the mesoporous thin films of transition metal oxides with accessible pores from the film surfaces can be used for long sought applications such as photocatalysis, photovoltaics and membranes.

This research was financially supported by KOSEF (SRC, CNNC). We thank Mr J. S. Ju at Central Research Facilities, SKKU for the TEM data.

Notes and references

† For the TEM studies, the nanoparticles were embedded into a polyacrylamide matrix by refluxing with added acrylamide.

1 Y. Matsumoto, Y. Ishikawa, M. Nishida and S. Ii, *J. Phys. Chem. B*, 2000, **104**, 4204; E. Stathatos, D. Tsiourvas and P. Lianos, *Colloids Surf. A*, 1999, **149**, 49.

2 A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.*, 2000, **33**, 269; F. G. Gao, A. J. Bard and L. D. Kispert, *J. Photochem. Photobiol. A: Chem.*, 2000, **130**, 49.

3 F. M. Vichi, M. I. Tejedor-Tejedor and M. A. Anderson, *Chem. Mater.*, 2000, **12**, 1762.

4 D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2014; D. M. Antonelli, *Microporous Mesoporous Mater.*, 1999, **30**, 315; V. F. Stone. Jr. and R. J. Davis, *Chem. Mater.*, 1998, **10**, 1468; D. T. On, *Langmuir*, 1999, **15**, 8561; D. Khushalani, G. A. Ozin and A. J. Kuperman, *J. Mater. Chem.*, 1999, **9**, 1491; G. de A. A. Soler-Illia and C. Sanchez, *New J. Chem.*, 2000, **24**, 493.

5 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 6707.

6 H. K. Park, D. K. Kim and C. H. Kim, *J. Am. Ceram. Soc.*, 1997, **80**, 743; C. Sanchez, J. Livage, M. Henry and F. Babonneau, *J. Non-Cryst. Solids*, 1988, **100**, 65.

7 L. Brus, *J. Phys. Chem.*, 1986, **90**, 2555; C. Kormann, P. W. Bahnemann and M. R. Hoffmann, *J. Phys. Chem.*, 1988, **92**, 5196.