

Formation of Highly Ordered Mesoporous Titania Films Consisting of Crystalline Nanopillars with Inverse Mesospace by Structural Transformation

Chia-Wen Wu,[†] Tetsu Ohsuna,^{‡,§} Makoto Kuwabara,[‡] and Kazuyuki Kuroda^{*,†,‡,§}

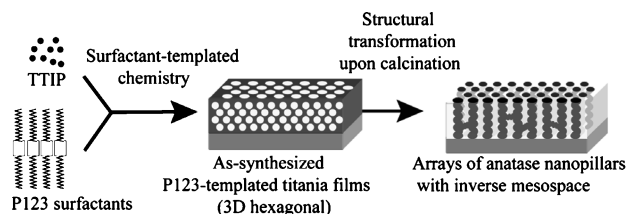
Department of Applied Chemistry, Graduate School of Science and Engineering, and Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo 169-8555, Japan, CREST, Japan Science and Technology Agency, Honcho 4-1-8, Kawaguchi-shi, Saitama 332-0012, Japan, and Department of Applied Science for Electronics and Materials, Kyushu University, 6-1 Kasuga-kouen, Kasuga, Fukuoka 816-850, Japan

Received January 20, 2006; E-mail: kuroda@waseda.jp

This paper reports a very unique structural transformation process for a new nanostructured titania film consisting of high-density anatase nanopillars with open-spaced, perpendicular, and continuous porosity (referred to as inverse mesospace). Ordered crystalline mesoporous titania films have been synthesized by utilizing surfactants as structure-directing agents,¹ and these materials have received great interests because of their adsorption abilities and semiconducting properties.² The mesostructures reported so far have included 2D hexagonal with mesochannels running parallel to substrates^{3a} and 3D cubic structures.^{3b,c} Although these mesostructures exhibit ordered pore size and high surface area, the lack of perpendicular porosity greatly reduces the merit of the films. Therefore, the crystalline titania films with perpendicular porosity have been highly demanded because this pore configuration should increase the accessibility and enhance the efficiencies of adsorption and catalysis.

Structural transformation of mesoporous titania films upon calcination can be regarded as an alternative method to produce new structures because contraction of the mesostructure along the direction perpendicular to substrates preferentially occurs during the thermal processes. For example, rectangular and grid-like structures can be derived from 2D hexagonal and 3D cubic structures, respectively.⁴ The evolution of crystallinity upon calcination has also been studied.⁵ However, a titania film with both crystalline TiO₂ phase and perpendicular porosity has never been reported yet. Here we report the structural transformation of a 3D hexagonal titania film with its *c* axis perpendicular to the substrate. The obtained titania film exhibits a unique morphology, that is, high-density crystalline TiO₂ anatase nanopillars are surrounded by inverse mesospace, as shown in Scheme 1.

Scheme 1. An Illustration for the Synthesis Process of the Titania Film Consisting of Crystalline Nanopillars with Inverse Mesospace



Titanium tetraisopropoxide (TTIP) was used as a titanium source, and HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H (Pluronic P123) was used as a template. The final solution with the composition of 1 TTIP/0.01 P123/17.6 EtOH/1.9 HCl/7.2 H₂O (in

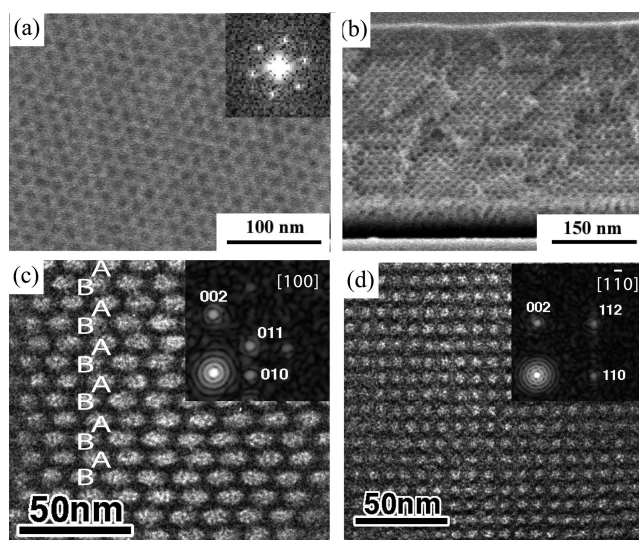


Figure 1. (a) Top and (b) cross-sectional HR-SEM images, and (c) and (d) cross-sectional TEM images of the as-synthesized P123-templated titania film; (c) and (d) were viewed from the [100] and [1-10] zone axes of the 3D hexagonal structure, respectively.

molar ratio)⁶ was spin coated on silicon substrates. The as-coated films were then aged at -20 °C for 24 h. After aging, the films were heated at a ramp rate of 1 °C/min to various temperatures (100–400 °C) and kept at the temperatures for 4 h.

The mesostructure of the as-synthesized titania film was determined as a 3D hexagonal structure with an ABAB stacking on the basis of the HR-SEM and TEM results.⁷ The HR-SEM images demonstrate that the film exhibits an ordered honeycomb arrangement over the entire top surface (Figure 1a) and a 2D ordered structure in the cross section (Figure 1b), demonstrating that the film has a 3D structure. The cross-sectional TEM images of the film show an ABAB stacking sequence (Figure 1c) and a tetragonal organization (Figure 1d) that can be regarded as viewed from [100] and [1-10] zone axes, respectively. The corresponding FFT diffractograms are shown in the insets. Reflection conditions (extinction rules) retrieved from the diffractograms are (i) 00*l*, *l* = 2*n*; (ii) 0*kl*, no condition; (iii) *hhl*, *l* = 2*n*. Assuming the unit cell is hexagonal, the reflection conditions correspond to those of the space groups of *P6₃mc*, *P6₂c*, and *P6₃/mmc*. Since the TEM images of Figure 1c and d show 2D symmetry of *pmg* and *pmm*, respectively, we chose *P6₃/mmc* as the most suitable space group for the 3D hexagonal structure with the lattice parameters *a* = *b* = 17 nm and *c* = 20 nm, and the *c* axis of the 3D hexagonal structure is perpendicular to the substrate.⁸

After calcination at 400 °C, the 3D hexagonal structure was transformed to the arrays of titania pillars, as shown by the SEM

[†] Graduate School of Science and Engineering, Waseda University.

[‡] Kagami Memorial Laboratory for Materials Science and Technology, Waseda University.

[§] CREST.

[†] Kyushu University.

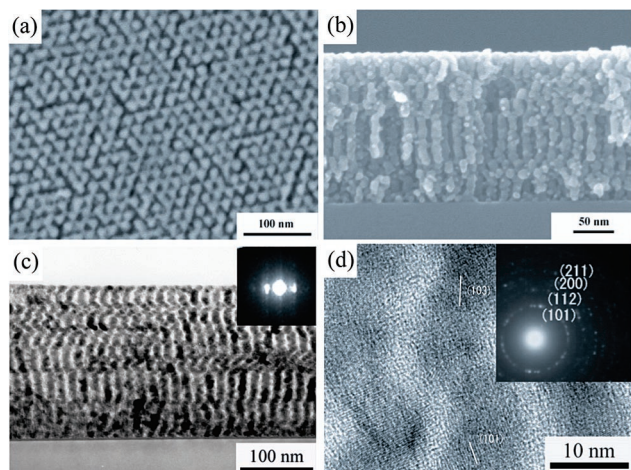


Figure 2. (a) Top and (b) cross-sectional HR-SEM images, and (c) and (d) cross-sectional HR-TEM images of the P123-templated titania film after calcination at 400 °C. ED pattern is shown in the inset.

images (Figure 2a and b). The cross-sectional TEM image (Figure 2c) and its corresponding electron diffraction (ED) pattern in the inset reveal that the calcined film consists of ordered titania nanopillars and perpendicular mesospace. The XRD pattern of the calcined film proves the formation of anatase phase (Figure S2). In addition, the HR-TEM image (Figure 2d) and the selected area ED pattern (Figure S3) indicate that the titania pillars are polycrystalline (anatase nanocrystallites of ca. 2–13 nm in diameter). Some nanocrystallites fused together and aligned along the c axis of the initial 3D hexagonal structure.

The nanopillars in the film are periodically distributed and partially interconnected with each other, leading to the formation of porosity (Figure 2a). This porosity can be regarded as “inverse mesospace” of a 2D hexagonal structure with “mesochannels” running perpendicular to the substrate (Scheme S1). The N_2 adsorption–desorption data display a type-IV isotherm, indicative of mesoporosity (Figure S4),⁹ and the BET surface area was calculated to be $58 \text{ m}^2 \text{ g}^{-1}$. Although arrays of titania pillars have been fabricated by lithography and electrochemical etching processes,¹⁰ the process presented here provides pillars with a smaller period.

The mechanism of the structural transformation of the 3D hexagonal titania film is explained as follows. The transformation is supposed to be induced by the large contraction of the film (about 40%) in the perpendicular direction and the crystallization of the framework during the thermal processes. As viewed from the [100] zone axis (cross-sectional view, Figure 3a), the 3D hexagonal structure shows an alternatively organized ABAB stacking of the porous layers (spherical white and gray, respectively) surrounded by amorphous titania (black area). We found that a great contraction in the direction perpendicular to the substrate occurred when the as-synthesized film was calcined at 200 °C (Figure S5). This large contraction of the film caused the merging of pores along the c axis of the initial 3D hexagonal structure, leading to the inverse mesospace in the final structure.

As viewed from the [001] zone axis (top surface view, Figure 3b), the areas marked as “Ti” are the regions of titania existing throughout the film thickness. Upon the calcination, the amorphous titania in the Ti areas shrink along the c axis of the 3D hexagonal structure (the direction normal to the paper) and crystallize into the anatase phase. These areas are the positions where the final nanopillars formed, as evidenced by the fact that the interval of the pores (ca. 17 nm) before calcination is almost same as that of the TiO_2 nanopillars after calcination (ca. 16 nm). At the present stage, we consider that both the structure of 3D hexagonal and the

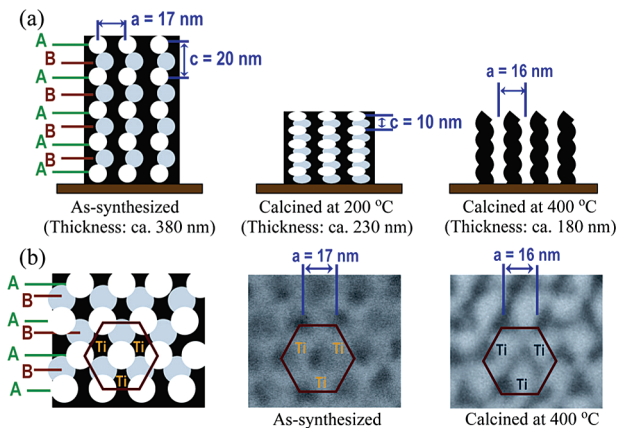


Figure 3. Plausible mechanism for the structural transformation of the 3D hexagonal structure viewed from (a) cross section and (b) top surface.

nature of titania are important for the structural transformation under the present conditions.

In conclusion, a new nanostructured titania film consisting of crystalline nanopillars has been produced for the first time via structural transformation of a 3D hexagonal phase. The film of crystalline TiO_2 nanopillars with inverse mesospace is expected to have potential applications for photocatalysts and optical-electronic devices with improved performances.

Acknowledgment. We thank Mr. M. Fujiwara (Kagami Memorial Lab) for HR-TEM, and Prof. Y. Honda and Dr. H. S. Yun (ASMeW) for the help with HR-SEM. This work is supported in part by Grants-in-Aid for the 21st Century COE Program “Practical Nano-Chemistry” and the Encouraging Development Strategic Research Centers Program “Establishment of Consolidated Research Institute for Advanced Science and Medical Care” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). The A3 Foresight Program “Synthesis and Structural Resolution of Novel Mesoporous Materials” supported by the Japan Society for Promotion of Science (JSPS) is also acknowledged.

Supporting Information Available: Experimental section, illustration of inverse mesospace, XRD and TEM results for the determination of the 3D hexagonal structure, XRD and HR-SEM data of the films calcined at various temperatures, N_2 adsorption–desorption isotherm of the film calcined at 400 °C, and complete ref 4b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Soler-Illia, G. J. de A. A.; Crepaldi, E. L.; Grosso, D.; Sanchez, C. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 109–126.
- (2) (a) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49–68. (b) *TiO₂ Photocatalysis*; Fujishima, A., Hashimoto, K., Watanabe, T., Eds.; BKC Inc.: Tokyo, Japan, 1999.
- (3) (a) Yun, H. S.; Miyazawa, K.; Zhou, H. S.; Honma, I.; Kuwabara, M. *Adv. Mater.* **2001**, *13*, 1377–1380. (b) Alberius, P. C. A.; Frindell, K. F.; Hayward, R. C.; Kramer, E. J.; Stucky, G. D.; Chmelka, B. F. *Chem. Mater.* **2002**, *14*, 3284–3294. (c) Crepaldi, E. L.; Soler-Illia, G. J. de A. A.; Grosso, D.; Cagnol, F.; Ribot, F.; Sanchez, C. *J. Am. Chem. Soc.* **2003**, *125*, 9770–9786.
- (4) (a) Grosso, D.; Soler-Illia, G. J. de A. A.; Babonneau, F.; Sanchez, C.; Albouy, P. A.; Brunet-Bruneau, A.; Balkenende, A. R. *Adv. Mater.* **2001**, *13*, 1085–1090. (b) Grosso, D.; et al. *Chem. Mater.* **2003**, *15*, 4562–4570.
- (5) Kirsch, B. L.; Richman, E. K.; Riley, A. E.; Tolbert, S. H. *J. Phys. Chem. B* **2004**, *108*, 12698–12706.
- (6) The detailed synthesis method is described in Supporting Information.
- (7) The detailed structural characterization of the 3D hexagonal phase is described on page S2 and Figure S1 in Supporting Information.
- (8) Miyata, H.; Suzuki, T.; Fukuoka, A.; Sawada, T.; Watanabe, M.; Noma, T.; Takada, K.; Mukaide, T.; Kuroda, K. *Nat. Mater.* **2004**, *3*, 651–656.
- (9) Kruk, M.; Jaroniec, M. *Chem. Mater.* **2001**, *13*, 3169–3183.
- (10) (a) Shimada, S.; Miyazawa, K.; Kuwabara, M. *Jpn. J. Appl. Phys.* **2002**, *41*, L291–L293. (b) Masuda, H.; Kanezawa, K.; Nakao, M.; Yokoo, A.; Tamamura, T.; Sugiura, T.; Minoura, K. *Adv. Mater.* **2003**, *15*, 159–161.

JA060453P