Synthesis of transparent thick film of mesoporous TiO_2 by solvent evaporation method

S. NAGAMINE*, S. TAKAHASHI, E. SASAOKA
Department of Environmental Materials & Chemistry, Faculty of Environmental Science & Technology, Okayama University, 3-1-1, Tsushima-Naka, Okayama 700-8530, Japan
E-mail: shinsuke@cc.okayama-u.ac.jp

Mesoporous TiO_2 is an attractive material for its high photocatalytic activity. Fabrications of mesoporous materials have been extensively studied in the last decade. In particular, the surfactant-templating method has attracted the main attention of those works. It is noted that the macroscopic morphology of the mesoporous materials is also quite important for their practical use. The macroscopic morphology strongly depends on the synthesis route. For example, the product becomes necessarily powder when produced via the precipitation from the precursory solution [1–3]. On the other hands, thin films can be synthesized by the coating of TiO_2-template sols on substrates [4, 5]. For the present, the synthesis of mesoporous bulk solid is still a challenging problem.

In earlier works, the authors synthesized the submillimeter-thick transparent films of mesoporous silica by the solvent evaporation method [6, 7]. In these works, the starting silica sol containing surfactant was converted to the gel by the evaporation of solvent. As the solvent evaporated, the cooperative formation of silica-surfactant nanostructure was promoted because of the increase in the concentration of templating surfactant. We found that controlling the gelation rate by adjusting the water and catalytic acid concentrations was essential for the successful formation of the ordered hexagonal mesostructure. In this work, this method was applied for the synthesis of transparent film of mesoporous TiO_2, which is expected to find applications in the photochemical uses.

The mesoporous TiO_2 film was prepared in the following procedures: 0.58 g of triblock copolymer ($(EO)_x(PO)_y(EO)_z$, M_w: 5800, Aldrich) as a template was dissolved in 10.0 g of ion-exchanged water. On addition of 10.0 g of HCl aqueous solution (2.0 mol/1) and 2.84 g of titanium tetraisopropoxide (TTIP, Wako Pure Chemical Industries, Ltd.) to the triblock copolymer solution, white precipitates were formed due to the immediate hydrolysis of TTIP. The molar ratio of template to TTIP was 0.01. The precipitate–solvent mixture turned to transparent TiO_2-template sol due to the presence of HCl during the aging at 278 K for 10 hr. Then, the sol was transferred to a Teflon petri dish (i.d. = 101 mm) and dried at 313 K for a day to complete the gelation. The film cracked into small pieces on completion of drying, peeled off the dish and was calcined at 673 K in air for 3 hr to remove the template. The sample for comparison was prepared by the same procedure except for the absence of triblock copolymer.

Fig. 1a shows a photograph of templated films, which are transparent and several millimeters in width. The thickness of the film is ca. 80 μm as shown in Fig. 1b. The non-templated film has thickness of ca. 40 μm, smaller than that of templated one. This noteworthy difference in thickness is due their porosity, as shown by the nitrogen adsorption measurements in the following.

Fig. 2a shows the nitrogen adsorption/desorption isotherms of the templated and non-templated films at 77 K (BEL Japan, Inc., BELSORP 28SA). The both isotherms show steep increase in the adsorbed volume due to the presence of uniform mesopores. The pore size distributions estimated by the Dollimore-Heal method are shown in Fig. 2b. The increases in pore size, pore volume and surface area (Table I) by the addition of triblock copolymer clearly shows its effect to template the mesopore structure, which is different from that of non-templated sample probably due to the aggregation of uniform-sized primary particles. The thickening of the film shown above is evidently due to the increase of the porosity.

The nanostructure and crystal structure were investigated by powder X-ray diffraction (Shimadzu XRD-5800). The small-angle XRD pattern of the templated sample presented no clear peak, showing that the uniform-sized mesopores confirmed by the nitrogen adsorption are not periodically arranged. The effect of the template on the crystal structure was also checked. The non-templated sample was composed of only the anatase crystal phase. The small portion of rutile phase coexisting with the main anatase phase was formed by the presence of triblock copolymer.

TABLE I Thickness, pore size, pore volume and surface area of each film

Template/TTIP (mol/mol)	Thickness (μm)	Pore size (nm)	Pore volume ($cm^3\,g^{-1}$)	Surface area ($m^2\,g^{-1}$)
0	40	4.5	0.066	78
10^{-2}	80	6.0	0.22	147

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*Author to whom all correspondence should be addressed.

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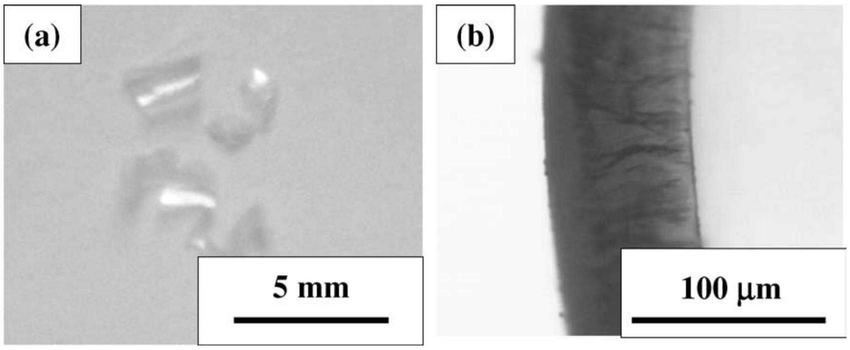

Figure 1 (a) Photograph and (b) optical microscope image (cross-section) of the templated films.

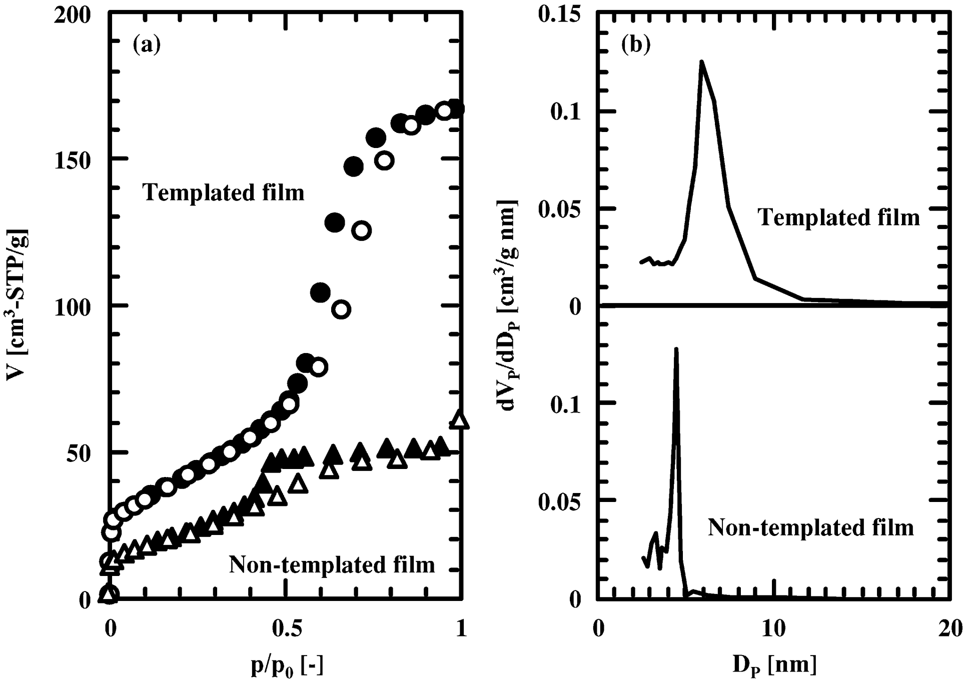

Figure 2 (a) Nitrogen adsorption/desorption isotherms and (b) pore-size distributions estimated by Dollimore-Heal method of the templated and non-templated films.

In summary, the transparent TiO_2 films with the thickness of several ten micrometers were synthesized by the solvent evaporation method from TiO_2 sol prepared in HCl acidic condition. The addition of triblock copolymer to the precursory sol resulted in the formation of developed mesopore structure.

Acknowledgments

This work was financially supported by Ministry of Education, Culture, Sports, Science and Technology of Japan through Grant-in-Aid for Young Scientists (No. 15710090). We are grateful to Prof. Ken-ichi Kurumada of Graduate School of Environmental and Information Sciences, Yokohama National University, for discussion.

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Received 9 September 2003
and accepted 29 January 2004