JOURNAL OF Materials CHEMISTRY Communication

Direct preparation of anatase TiO_2 nanotubes in porous alumina membranes

Hiroaki Imai, Yuko Takei, Kazuhiko Shimizu, Manabu Matsuda and Hiroshi Hirashima

Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku, Yokohama, 223-8522, Japan. E-mail: hiroaki@applc.keio.ac.jp

Received 26th July 1999, Accepted 25th October 1999

Monodisperse hollow nanocylinders consisting of crystalline titania particles have been directly prepared in a porous alumina membrane by a deposition technique using an aqueous solution system of titanium tetrafluoride.

Anodically grown alumina porous membranes have been used as templates for preparing nanoscale materials.[1–5] Since the diameter of the cylindrical pores of the membranes can be varied between 10 and 200 nm by altering the preparation conditions, the templating method has a number of interesting and useful features for the production of microscopically tailored materials. Solid or hollow microcylinders of desired materials, such as polymers,[1,2] metals,[1,2] carbons[3] and semiconductors,[4] have been obtained within cylindrical pores of uniform diameter in the membranes. However, preparing crystalline metal oxides in the nanopores of the membranes is difficult using conventional methods. Although Hoyer[4] electrochemically prepared titania nanotubes using a polymer mold having a negative structure of alumina porous membranes, the deposited titania was amorphous and calcination to induce crystallization led to deformation of the nanotubes. Moreover, this preparation method requires complicated processes including metal evaporation, polymer formation, dissolution of alumina, electrodeposition and dissolution of polymers. A direct deposition technique is desirable for the preparation of clearly shaped nanotubes consisting of crystalline metal oxides.

Recently, direct deposition using supersaturated solutions has been developed for the preparation of metal-oxide films such as silica,[6] titania,[7–9] vanadia[10] and tin oxide.[11] In particular, thin films consisting of well crystallized anatase particles are easily obtained from titanium tetrafluoride (TiF_4) solutions.[9] Using this technique, various substrates with complex shapes are coated with anatase through heterogeneous nucleation. Organic fibers, such as paper and cotton, have been successfully coated with small particles of anatase. Anatase titania is well known as a photocatalyst and as an electrode for wet-type photocells.[12–16] Since a highly porous material is required for photocatalytic applications, practical catalysts are usually prepared by coating the crystalline powder with organic binders. Since the anatase films deposited from TiF_4 solutions are mesoscopically porous, this direct deposition method is effective for the preparation of anatase photocatalysts.

Here, we describe the direct preparation of anatase nanotubules in nanochannels of porous alumina membranes using a deposition technique from TiF_4 solutions. The tubes obtained, which had cylindrical pores, were found to consist of anatase nanoparticles and contained mesoscale pores. Double-pore crystalline titania might be suitable for a variety of catalytic applications and filtration.

The precursor solution was prepared by dissolving TiF_4 (Aldrich) in purified water containing ammonia and stirred for 1 h. The pH and TiF_4 concentration of the solutions were adjusted to *ca.* 2.0 and 0.04 M, respectively. Porous alumina membranes (Whatman Anodisc 25) prepared electrochemically from aluminium metal were used as substrates. The membranes, which had straight channels of *ca.* 200 nm in diameter, were immersed in TiF_4 solution and maintained at 60 °C for 1–24 h. The substrate was removed by immersing in aqueous solutions of ammonia (pH 12) for several days at room temperature. The crystalline phase was identified by X-ray diffraction (XRD) using a Rigaku RAD-C system. The morphology and composition of the samples were observed using a scanning electron microscope (SEM, Hitachi S-2150) and a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700) equipped with an X-ray microanalyser. The specific surface area and pore-size distribution were estimated by N_2 adsorption using the BET and the BJH methods, respectively, using a Quantachrome Autosorb 1 apparatus. Titania deposited on cotton fibers was used for the N_2 adsorption to obtain a sufficient amount of sample for the estimation.

Following our previous study,[9] crystalline titania films (anatase phase) were deposited from aqueous solutions of TiF_4 at pH 1–3. The hydrolysis of TiF_4 in solution occurs in a stepwise manner to produce titania [eqn. (1)]:

$$TiF_4 \rightarrow Ti(OH)_{4-x}F_x \rightarrow TiO_2 \quad (1)$$

Thin films were prepared through heterogeneous nucleation on various types of substrates, such as glass, polyethylene and cotton fibers, since solutions under the used conditions become gradually supersaturated with titania produced by the stepwise reactions. On the other hand, precipitates were predominantly observed above pH 3 since such solutions became highly supersaturated with titania. Using this technique, anatase films were successfully deposited on the inner walls of alumina porous membranes. After dissolving the membrane, which was used as a substrate, using an aqueous solution of ammonia, the deposited titania films were obtained as nanotubes. Fig. 1 shows SEM and FE-SEM images of the nanotubes prepared in the nanochannels of the membranes. Surface analysis indicated that the alumina was completely removed by the basic solution. The walls of the tubes, with straight channels *ca.* 100–150 nm in diameter, were found to consist of small particles of size 10–20 nm. The channel diameter of the tubes was controllable over the range 50–150 nm by changing the deposition time. Finally, titania rods with no straight channels were obtained by deposition for >12 h. According to the XRD pattern shown in Fig. 2, the small particles forming the nanotubes are identified as anatase titania. The specific surface area of the deposited films was estimated to be 100–140 $m^2\,g^{-1}$. The particle size (10–15 nm) as calculated from the surface area is approximately equal to that evaluated from the SEM images. The diameter of the mesopores of the deposited anatase films was estimated to be in the range 5–10 nm. The mesopores arise from the spaces between the anatase particles. The tubes are thus characterized to be anatase cylinders having a bimodal pore distribution as shown in Fig. 3.

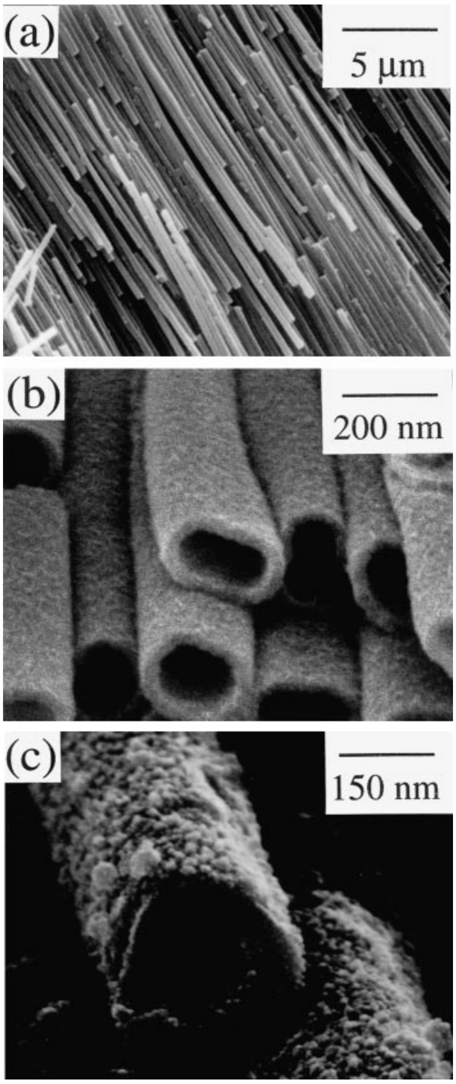

Fig. 1 SEM (a) and FE-SEM (b, c) images of titania nanotubes deposited from a TiF_4 solution (0.04 M, pH 2) at 60 °C for 1 h. The outside diameter is *ca.* 200 nm; the inside diameter is 100–150 nm.

The nanotubules were clearly produced by deposition of anatase films consisting of small particles on the inner walls of the nanochannels of the alumina membrane. Since the shape of the anatase tubes matched that of the nanochannels, deposition seems to have occurred through heterogeneous nucleation on the alumina surface. The precursor solutions supersaturated with titania directly produce crystal nuclei of anatase on the surface. Since Ti–F bonds are relatively stable, rapid hydrolysis and polymerization of the precursor molecules does not occur and such moderate reaction conditions lead to the deposition of stable crystalline particles on a substrate through heterogeneous nucleation. As a consequence, crystalline anatase nanotubes are directly obtained at a low temperature. Since no higher temperature annealing is required for crystallization, the tubular morphology and the pore sizes are clearly controlled by this technique.

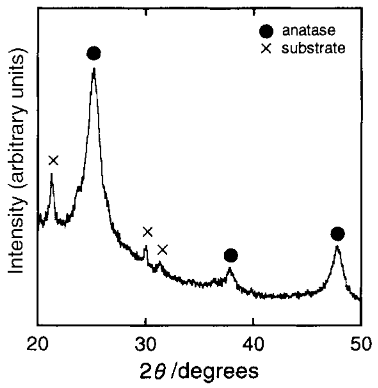

Fig. 2 An XRD pattern of titania nanotubes deposited from a TiF_4 solution (0.04 M, pH 2) at 60 °C for 1 h.

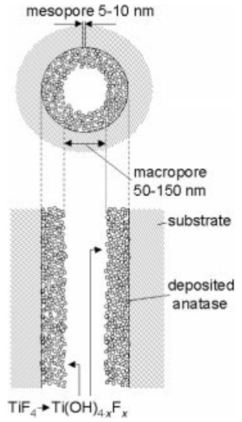

Fig. 3 A schematic model of deposition of anatase in a nanochannel and the bimodal pores of a nanotube.

The photocatalytic activity of the deposited anatase was examined by study of the oxidation reaction of nitrogen monoxide under illumination.[9] The as-deposited anatase was confirmed to show a similar performance to conventionally prepared anatase powder, although a considerable percentage of fluorine was detected on the films. Thus, anatase nanotubes with bimodal pore distribution are applicable as conventional and advanced photocatalysts. Moreover, highly tailored photocatalysts may be prepared by this technique since heat treatment, which causes deformation of nanopores, is not required.

Hollow anatase nanotubules with straight channels have been directly prepared from aqueous solutions of titanium tetrafluoride using alumina porous membranes as templates. The channel diameter was varied in the range 50–150 nm as a function of the deposition time. The wall of the tubes were evaluated to have nanopores of <10 nm. The morphology of the anatase nanotubes is highly controllable because no annealing for crystallization is required. The bimodal pores of the anatase nanotubes are extremely useful for various photocatalytic gas reactions and for filtration.

References

1 C. R. Martin, *Science*, 1994, **266**, 1961.
2 C. R. Martin, *Chem. Mater.*, 1996, **8**, 1739.
3 T. Kyotani, L. Tsai and A. Tomita, *Chem. Mater.*, 1996, **8**, 2109.
4 P. Hoyer, *Langmuir*, 1996, **12**, 1411.
5 H. Matsuda and K. Fukuda, *Science*, 1995, **268**, 1466.
6 H. Nagayama, H. Honda and H. Kawahara, *J. Electrochem. Soc.*, 1988, **135**, 2013.
7 S. Deki, Y. Aoi, O. Hiroi and A. Kajinami, *Chem. Lett.*, 1996, 433.
8 L. Baskaran, J. Song, Y. L. Liu, G. L. Chen and J. Graff, *J. Am. Ceram. Soc.*, 1998, **81**, 401.
9 K. Shimizu, H. Imai, H. Hirashima and K. Tsukuma, *Thin Solid Films*, 1999, **351**, 220.
10 S. Deki, Y. Aoi and A. Kajinami, *J. Mater. Sci.*, 1997, **32**, 4269.
11 K. Tsukuma, T. Akiyama and H. Imai, *J. Non-Cryst. Solids*, 1997, **210**, 48.
12 T. Ibusuki and K. Takeuchi, *J. Mol. Catal.*, 1994, **88**, 93.
13 H. Uchida, S. Itoh and H. Yoneyama, *Chem. Lett.*, 1993, 1995.
14 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
15 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
16 A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49.

Communication 9/06005G