JOURNAL OF MATERIALS SCIENCE **40** (2005) 5561–5563 LETTERS

Fabrication of three-dimensional ordered macroporous titanium oxide by the liquid-phase deposition method using colloidal template

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Recently, the fabrication of three-dimensional (3D) ordered porous materials has been of much interest [1]. Such materials have great potential in a variety of areas including photonics [2–4], catalysis [5], separation media [6, 7], and electrochemical applications. Of particular interest are dielectric 3D periodic structures that exhibit novel optical properties, potentially leading to optical filters, and photonic materials [2–4]. A widely used approach to the fabrication of 3D ordered porous materials is to fill the interstitial spaces of a colloidal template with the solid and subsequently to remove selectively the template materials [1]. Infiltration methods that have been employed include sol–gel method [8–10], electrodeposition [11–14], using suspensions of nanoparticles [15], and chemical vapor deposition (CVD) [2]. In this letter, we describe the use of the liquid-phase deposition (LPD) method to fabricate the 3D ordered macroporous TiO_2.

The LPD method is one of the wet processes and very unique process to deposit metal oxide thin films [16–20]. By using this method, it is possible to form metal oxide or hydroxide thin films homogeneously on various kinds of substrates, which are only immersed in the aqueous solution of a reactant. In this method, metal oxide or hydroxide thin films form by means of ligand-exchange (hydrolysis) equilibrium reaction of metal–fluoro complex species $M\mathrm{F}_x^{(x-2n)-}$ and the F^- consumption reaction with boric acid (H_3BO_3) or aluminum metal as an F^- scavenger. In the treatment solution, $M\mathrm{F}_x^{(x-2n)-}$ is hydrolyzed with water following ligand-exchange equilibrium reaction:

$$M\mathrm{F}_x^{(x-2n)-} + n\mathrm{H_2O} = \mathrm{MO}_n + x\mathrm{F}^- + 2n\mathrm{H}^+$$

The equilibrium reaction is shifted toward the right-hand side by the addition of boric acid (F^- ion scavenger), which readily reacts with F^- and forms a stable complex as follows:

$$\mathrm{H_3BO_3} + 4\mathrm{HF} = \mathrm{BF_4^-} + \mathrm{H_3O^+} + 2\mathrm{H_2O}$$

The addition of the F^- scavenger leads to the consumption of free F^- ions, and accelerates the ligand-exchange reaction. This method is very simple process and does not require any special equipment. The advantage of utilizing the LPD method to fabricate the 3D macroporous material is that the metal oxide or hydroxide directly forms as solid phase from liquid phase. The interstitial spaces of a colloidal template are completely filled by solution and then metal oxide forms onto the whole colloidal template surface in contact with solution. The deposition fills the interstitial spaces from whole surface, which improves completeness of infilling. We demonstrate here that the applicability of the LPD method using colloidal template as a substrate to fabricating 3D macroporous material. In this communication, we describe the method for fabricate 3D ordered macroporous titanium dioxide by the LPD method.

The parent solutions used for the LPD were aqueous solutions of $(NH_4)_2TiF_6$ and H_3BO_3. $(NH_4)_2TiF_6$ (Kishida Chemical Co. Ltd.) and H_3BO_3 (Nacalai Tesque Inc.) were dissolved in distilled water at a concentration of 0.5 mol dm^{-3}. These solutions were mixed to give a concentration of 0.1 mol dm^{-3} for $(NH_4)_2TiF_6$ and 0.2 mol dm^{-3} for H_3BO_3, and used for the deposition solution for the LPD method. The template we used was colloidal crystal assembled from polystyrene latex suspension by self-organized sedimentation on glass substrate [13]. The polystyrene latex (Sigma-Aldrich) sphere had an average diameter of 440 nm. The substrate covered with template was immersed and suspended vertically in the deposition solution, i.e., mixed solution of $(NH_4)_2TiF_6$ and H_3BO_3. The template adhered well to the substrate, and re-suspension of the latex particles to the deposition solution was not observed. Schematic procedure for fabrication of 3D ordered titanium oxide by the LPD method is illustrated in Fig. 1.

The morphology and microstructure of the fabricated macroporous titanium oxide films were observed by scanning electron microscope (SEM, JEOL JSM-6301F). Prior to observation by SEM, the samples were

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0022-2461 © *2005 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-4551-6

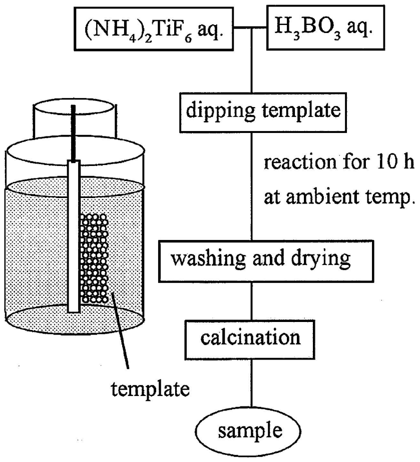

Figure 1 Schematic procedure of the fabrication of 3D ordered titanium oxide by the LPD process.

sputter coated with Au. X-ray diffraction measurements were performed on a Rigaku RINT-2500HFV using CuKα irradiation. Raman spectroscopy measurements were carried out on JEOL NRS-2100 with an argon laser (514.5 nm).

The deposition solution infiltrated into the interstitial spaces of the template when the template was immersed in the deposition solution, and then titanium oxide deposited by means of hydrolysis reaction of $(NH_4)_2TiF_6$ on the template surface, i.e., polystyrene latex surface. After reaction for 10 hr, the interstitial spaces of template were completely filled with titanium oxide. Fig. 2 shows SEM images of the template filled with the TiO_2. It can be seen that the polystyrene latex spheres are arranged in an ordered 3D hexagonal close packed structure and TiO_2 was deposited homogeneously. The top surface of the template was completely covered by deposited TiO_2 (Fig. 2a), because the deposition occurred on the whole surface of the individual polystyrene latex. Fig. 2b shows the SEM image of cleaved region of the sample. It can be clearly seen that the interstitial spaces between polystyrene latex spheres were completely filled with deposited TiO_2. The as-deposited sample was amorphous in X-ray diffraction, but Raman spectroscopy indicated that the infiltrated sample was anatase TiO_2 (Fig. 3).

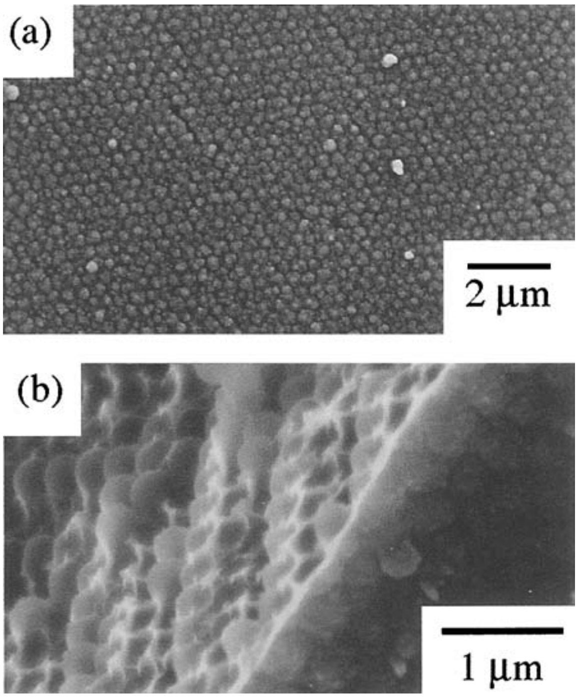

Figure 2 Scanning electron micrographs of polystyrene latex sphere template filled with TiO_2.

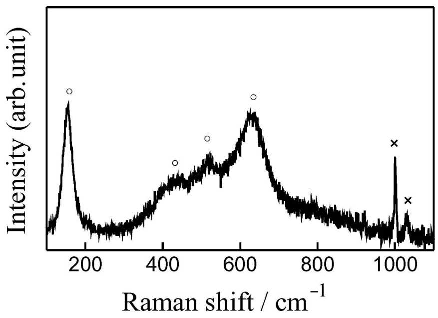

Figure 3 Raman spectrum of TiO_2-PS composite film. (○): anatase TiO_2, (×): polystyrene.

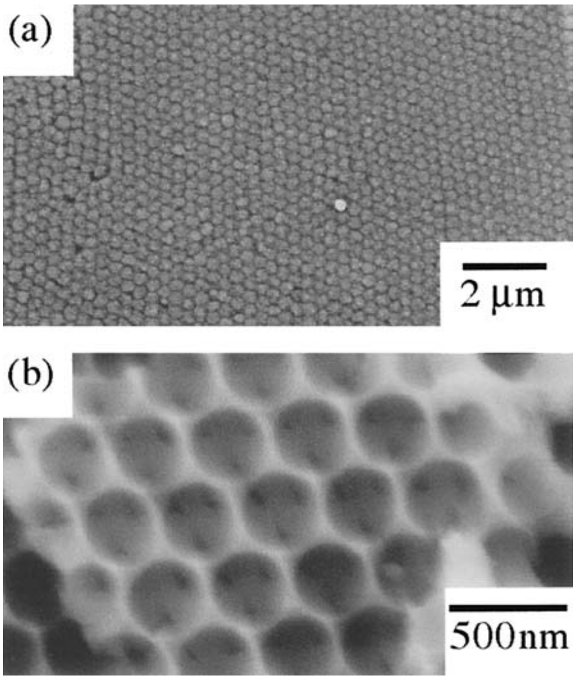

Figure 4 Scanning electron micrograph of 3D macroporous TiO_2 film.

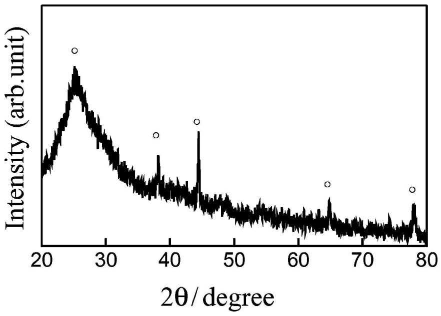

Figure 5 XRD pattern of 3D macroporous TiO_2 film. (○): anatase TiO_2.

In order to remove the template, the infiltrated samples were calcined in air. The calcination conditions, such as heating rate and temperature, is very important to fabricate well-ordered macoporous materials, because of the melting or outgassing of the templates and thermal expansion may break the ordered materials [21]. In this experiments the temperature was increased at a rate of 0.5 °C min^{-1} to 400 °C and stabilized at 400 °C for 1 hr before being decreased to ambient temperature. SEM images of the calcined sample are shown in Fig. 4. The top surface of the calcined sample was similar to that of infiltrated sample (Fig. 4a) and some cracks due to volume shrinkage during the calcination were observed. Fig. 4b shows the SEM image of peeled region of calcined sample in order to investigate internal voids of calcined sample. As shown in Fig. 4b, it can be clearly seen that periodic air spheres are surrounded by TiO_2. The average diameter of the air spheres is ∼327 nm compared with a diameter of polystyrene spheres of 440 nm. The interconnected openings, which correspond to points where the polystyrene sphere in the template were touching each other, were observed as dark spot within each pore. X-ray diffraction measurement of the calcined sample indicating that the sample becomes crystalline by the calcination, and the observed peaks are corresponded to anatase TiO_2 (Fig. 5).

In this communication, we have presented a novel method to fabricate 3D ordered macroporous TiO_2 by the LPD method. The LPD method using colloidal template provides simple and interesting route to fabricate 3D ordered macroporous metal oxides. The advantage of the LPD method is that this method can easily be adapted to other metal oxides and multi-component oxides. Until now, we have reported that several metal oxides and multi-component oxides thin films could be deposited by the LPD method [16–20]. Currently the fabrication of other metal oxides and multi-component oxides is being undertaken using the LPD method with colloidal template.

References

1. C. F. BLANFORD, H. YAN, R. C. SCHRODEN, M. AL-DAOUS and A. STEIN, *Adv. Mater.* **13** (2001) 401; A. STEIN, *Macropor. Mesopor. Mater.* **44/45** (2001) 227.
2. A. A. ZAKHIDOV, R. H. BAUGHMAN, Z. IQBAL, C. CUI, I. KHAYRULLIN, S. O. DANTAS, J. MARTI and V. G. RALCHENKO, *Science* **282** (1998) 897.
3. R. C. SCHRODEN, M. AL-DAOUS and A. STEIN, *Chem. Mater.* **13** (2001) 2945.
4. M. S. THIJSSEN, R. SPRIK, J. E. G. J. WIJNHOVEN, M. MEGENS, T. NARAYANAN, A. LAGENDIJK and W. L. VOS, *Phys. Rev. Lett.* **83** (1999) 2730.
5. P. T. TANEV, M. CHIBWE and T. J. PINNAVAIA, *Nature* **368** (1994) 321.
6. K. LEWANDOWSKI, P. MURER, F. SVEC and J. M. J. FRECHET, *Anal. Chem.* **70** (1998) 1629.
7. D. B. AKOLEKAR, A. R. HIND and S. K. BHARGAVA, *J. Colloid Interface Sci.* **199** (1998) 92.
8. A. IMHOF and D. J. PINE, *Nature* **389** (1997) 948.
9. Y.-H. YE, S. BADILESCU and V.-V. TRUONG, *Appl. Phys. Lett.* **81** (2002) 616.
10. R. C. SCHRODEN, M. AL-DAOUS, C. F. BLANFORD and A. STEIN, *Chem. Mater.* **14** (2002) 3305.
11. P. N. BARTLETT, P. R. BIRKIN and M. A. GHANEM, *Chem. Commun.* (2000) 1671.
12. P. V. BRAUN and P. WILTZIUS, *Adv. Mater.* **13** (2001) 482.
13. P. N. BARTLETT, J. J. BAUMBERG, P. R. BIRKIN, M. A. GHANEM and M. C. NETTI, *Chem. Mater.* **14** (2002) 2199.
14. L. XU, W. L. ZHOU, C. FROMMEN, R. H. BAUGHMAN, A. A. ZAKIHOV, L. MALKINSKI, J.-Q. WANG and J. B. WILEY, *Chem. Commun.* (2000) 997.
15. Q.-B. MENG, C.-H. FU, Y. EINAGA, Z.-Z. GU, A. FUJISHIMA and O. SATO, *Chem. Mater.* **14** (2002) 83.
16. S. DEKI, Y. AOI, O. HIROI and A. KAJINAMI, *Chem. Lett.* (1996) 433.
17. S. DEKI, Y. AOI, H. YANAGIMOTO, K. ISHII, K. AKAMATSU, M. MIZUHATA and A. KAJINAMI, *J. Mater. Chem.* **6** (1996) 1879.
18. S. DEKI, Y. AOI, Y. MIYAKE, A. GOTOH and A. KAJINAMI, *Mater. Res. Bull.* **31** (1996) 1399.
19. S. DEKI and Y. AOI, *J. Mater. Res.* **13** (1998) 883.
20. S. DEKI, Y. IIZUKA, K. AKAMATSU, M. MIZUHATA and A. KAJINAMI, *J. Mater. Chem.* **44** (2001) 984.
21. H. YAN, C. F. BRANFORD, J. C. LYTLE, C. B. CARTER, W. H. SMYRL and A. STEIN, *Chem. Mater.* **13** (2001) 4314.

Received 11 August 2004
and accepted 9 May 2005