Biomimetic Approach for Exact Control of TiO_2 Periodic Microstructures

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Periodic array of titanium dioxide (TiO_2) microprojections was fabricated in aqueous solutions using poly(methylmethacrylate) (PMMA) films with ordered microcavities as a mold. The periodic microprojections consisting of crystalline TiO_2 exquisitely transcribed the architecture of the mold without deformation or shrinkage. This biomimetic route including preferable nucleation on the specific organic surface and subsequent growth of the crystalline phase at a low temperature is applicable to construct three-dimensional periodic architectures for photonic structures of various metal oxides.

Three-dimensional periodic structures ranged over micro- and nanometer scales are valuable for photonic crystals. Opaline lattice of silica (SiO_2)[1,2] and polystyrene (PS)[3,4] spheres prepared with suspensions of monodispersed colloidal particles by self-assembly is an example of the photonic structures with periodic microstructures. Lithography,[5,6] anordization[7] and etching[8] techniques with micropatterned masks were also applied to fabrication of the structures to obtain tailored optical functions. Well-ordered architectures were also prepared by templating techniques using these periodic structures as a mold.[1–11] Transcription is achieved by embedment of a desired material into the periodic voids of the molds. Infiltration of inorganic materials, such as metals,[1,5] carbons,[2,10] chalcogenides[6] and sulfides,[9] was carried out by diverse techniques, such as electrodeposition,[1,6] chemical vapor deposition (CVD)[2,10] and spray pyrolysis.[11] However, nonconductive, processable and inexpensive organic materials are not available as a mold because conductive substrates or high processing temperatures were required in these deposition routes. Replication of the periodic structures with transparent metal oxides was studied by infiltrating the oxide precursors into the microchannels by sol-gel methods.[4–6] In these cases, the short-range shapes within several micrometers were replicated with the metal oxides. However, the long-range structures including the periodicity were deformed due to shrinkage during densification and/or crystallization on drying and firing processes. Wijinhoven et al.[3] reported that the periodicity of the replicated structure with oxide was above 30% less than that of the original mold by shrinkage. Exact replication leading control of the morphology and periodicity is essential for the functional photonic applications. Thus, a novel fabrication technique is required for exact replication of well-ordered periodic patterns of organic molds with dense and crystalline metal oxides.

Many organisms produce inorganic materials having well-ordered tissues with their proper organic matrices. Shells and pearls are composed of periodically layered architectures of calcium carbonates and proteins.[12] Nanoscaled particles of magnetite (Fe_3O_4) enveloped with lipid bilayer are intercellularly produced by magnetic bacteria.[13] The magnetite particles grown within the organic membranes have high homogeneousness in the morphology, size, and magnetic characteristic. In the biomineralization, strict control of the morphology through nucleation on a proper surface and crystal growth in a restricted cavity of organic matrix in a supersaturated aqueous solution is indispensable.[14] Recently, low-temperature processes mimicking the biological activity have been developed for preparation of various metal oxide films.[15–21] We previously obtained crystalline TiO_2 having complex shapes with biomimetic processes using supersaturated aqueous solutions and organic templates, such as cotton fibers[22] and plant veins.[23] The resultant TiO_2 structures exquisitely replicated the negative shapes of the templates. In the present work, we achieved exact replication of the micromorphology of an organic mold with crystalline TiO_2 by applying the biomimetic approach. The long-range periodicity of the mold was strictly transcribed into the metal oxide.

PMMA films prepared by coating X-ray sensitive PMMA resist (Tokyo Ohka Kogyo, OEBR-1000) on a silicon wafer were used as an organic mold. The oleophilic organic surface is suitable for heterogeneous nucleation of TiO_2 crystals in $TiOSO_4$ aqueous solutions.[17,18] Periodic cavities in PMMA films were fabricated by exposure to an X-ray beam from synchrotron radiation (SR) through a microchannelplate™ (Hamamatsu Photonics) as a photomask and subsequent chemical etching with methylethylketon at room temperature. The exposure was performed with SR of 750 MeV through a beryllium window at the irradiation quantity of 30 mA·h. PMMA molds having the periodic microcavities were immersed in a precursor solution for TiO_2 deposition. An acidic aqueous solution prepared with $TiOSO_4$ was used as a precursor solution. The supersaturated condition for the deposition of the crystalline phase was achieved according to Refs. 17 and 18. After ultrasonication for degassing the microcavities, crystalline TiO_2 was gradually grown on the PMMA surface through heterogeneous nucleation at 60 °C (Figs. 1a and 1b). Then, the microcavities were completely infiltrated

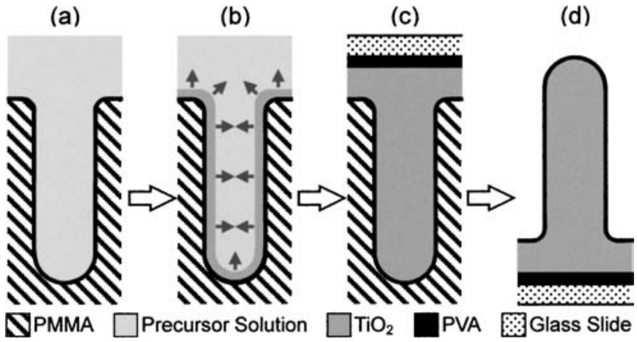

Figure 1. Schematic process for preparation of a TiO_2 microprojection with a supersaturated aqueous solution and PMMA mold.

with crystalline TiO_2 after about 1 week (Fig. 1c). The TiO_2-loaded PMMA molds were rinsed with purified water and dried at room temperature. A glass slide was bound on the top surface of the TiO_2-loaded template with poly(vinyl alcohol) aqueous solution as a binder. Periodic TiO_2 microprojections were obtained on the glass slide by dissolving PMMA with ethyl acetate (Fig. 1d).

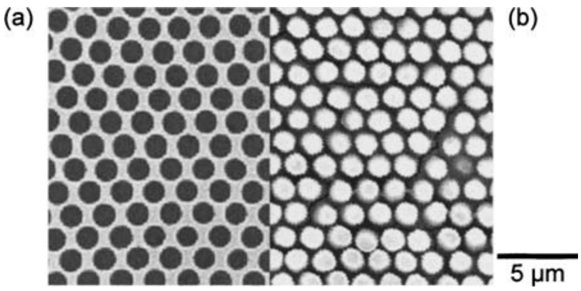

Figure 2. FESEM micrographs of a PMMA mold (a) and as-prepared TiO_2 microprojection replicating the morphology of a mold (b). The crystal phase of TiO_2 shown in (b) was anatase.

Figures 2 shows FESEM micrographs of a PMMA mold before application (a) and crystalline TiO_2 microprojections with the negative shape of the mold (b). The TiO_2 microprojections strictly transcribed the periodicity of the microcavities of the PMMA mold. Deformation due to shrinkage in this process was negligible because rigid framework consisting of crystalline TiO_2 was directly produced without heat treatment. As shown in Figs. 3a and 3b, the morphology of the TiO_2 microprojections was also controlled exquisitely with the shape of the cavities. The height of the projections was controlable by changing the depth of the cavities of the molds[24] (Figs. 3c and 3d). The smooth surface of the projections indicates that heterogeneous nucleation of crystalline TiO_2 was facilitated on the oleophilic surface of the PMMA molds. The exact transcription is achieved by direct growth of the crystalline oxide in the microcavities of the organic molds having a specific surface for TiO_2 nucleation. In contrast, deformation of the periodic structures produced by conventional sol-gel methods is an essential problem for the morphological control. Heat treatment is commonly needed for formation of rigid and dense crystalline structures because the sol-gel products are amorphous and contain a great amount of impurities, such as water and organics. The biomimetic approach without post annealing is applicable for various kinds of metal oxide materials. Moreover, three-dimensionally ordered microarchitectures would be replicated with crystalline oxides by controlling the supersaturated condition and the surface for the heterogeneous nucleation. Thus, the novel technique has a great potential for fabrication of well-tailored photonic structures using organic molds.

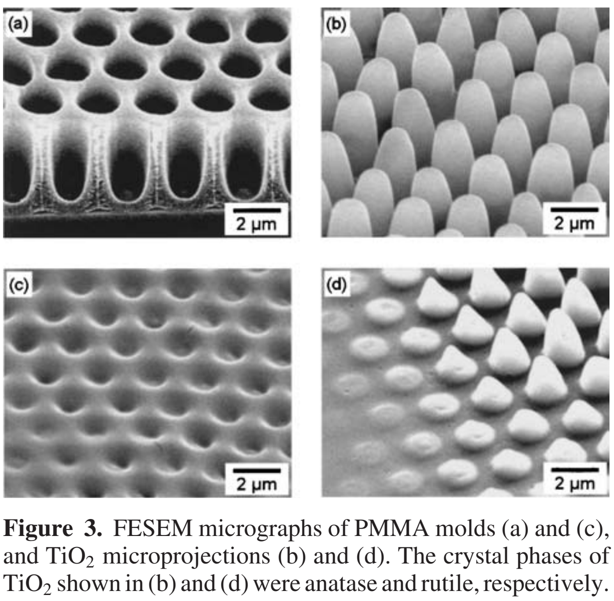

Figure 3. FESEM micrographs of PMMA molds (a) and (c), and TiO_2 microprojections (b) and (d). The crystal phases of TiO_2 shown in (b) and (d) were anatase and rutile, respectively. The tilt angle for the FESEM observation is 45°.

References and Notes

1 J. E. G. J. Wijnhoven, S. J. M. Zevenhuizen, M. A. Hendriks, D. Vanmaekelbergh, J. J. Kelly, and W. L. Vos, *Adv. Mater.*, **12**, 888 (2000).
2 A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti, and V. G. Ralchenko, *Science*, **282**, 897 (1998).
3 J. E. G. J. Wijnhoven and W. L. Vos, *Science*, **281**, 802 (1998).
4 B. Gates, Y. Yin, and Y. Xia, *Chem. Mater.*, **11**, 2827 (1999).
5 C. Cuisin, A. Chelnokov, and J. M. Lourtioz, *J. Vac. Sci. Technol.*, *B*, **18**, 3505 (2000).
6 I. B. Divliansky, A. Shishido, I. C. Khoo, T. S. Mayer, D. Pena, S. Nishimura, C. D. Keating, and T. E. Mallouk, *Appl. Phys. Lett.*, **79**, 3392 (2001).
7 H. Masuda and K. Fukuda, *Science*, **268**, 1466 (1995).
8 T. Tada, V. V. Poborchii, and T. Kanayama, *Jpn. J. Appl. Phys.*, **38**, 7253 (1999).
9 H. Míguez, A. Blanco, C. López, F. Meseguer, H. M. Yates, M. E. Pemble, F. López-Tejeira, F. J. García-Vidal, and J. Sanchez-Dehesa, *J. Lightwave Technol.*, **17**, 1975 (1999).
10 S. Okuyama, S. I. Matsushita, and A. Fujishima, *Chem. Lett.*, **2000**, 534.
11 S. Matsushita, T. Miwa, and A. Fujishima, *Chem. Lett.*, **2000**, 925.
12 C. M. Zaremba, A. M. Belcher, M. Fritz, S. Mann, P. K. Hansma, D. E. Morse, J. S. Speck, and G. D. Stuckky, *Chem. Mater.*, **8**, 679 (1996).
13 T. Matsunaga and T. Sakaguchi, *J. Biosci. Bioeng.*, **90**, 1 (2000).
14 S. Mann, *Nature*, **365**, 499 (1993).
15 H. Nagayama, H. Honda, and H. Kawahara, *J. Electrochem. Soc.*, **135**, 2013 (1988).
16 S. Deki, Y. Aoi, O. Hiroi, and A. Kajinami, *Chem. Lett.*, **1996**, 433.
17 S. Yamabi and H. Imai, *Chem. Lett.*, **2001**, 220.
18 S. Yamabi and H. Imai, *Chem. Mater.*, **14**, 609 (2002).
19 K. Tsukuma, T. Akiyama, and H. Imai, *J. Non-Cryst. Solids*, **210**, 48 (1997).
20 S. Deki, Y. Aoi, J. Okibe, H. Yanagimoto, A. Kajinami, M. Mizuhata, *J. Mater. Chem.*, **7**, 1769 (1997).
21 S. Deki, Y. Aoi, and A. Kajinami, *J. Mater. Sci.*, **32**, 4269 (1997).
22 H. Imai, M. Matsuta, K. Shimizu, H. Hirashima, and N. Negishi, *J. Mater. Chem.*, **10**, 2005 (2000).
23 H. Imai, K. Shimizu, M. Matsuta, and H. Hirashima, *Solid State Ionics*, in press.
24 The depth of the cavities was controlled by changing the intensity of SR.