Bull. Chem. Soc. Jpn. Vol. 80, No. 6, 1226–1228 (2007)

Rapid Fabrication of a Smooth Hollow-Spheres Array

Sachiko Matsushita,[1,4] Shigenori Fujikawa,[2]
Shinya Onoue,[2] Toyoki Kunitake,[2]
and Masatsugu Shimomura*[1,3]

[1]Dissipative-Hierarchy Structures Laboratory,
RIKEN Frontier Research System,
2-1 Hirosawa, Wako 351-0198

[2]Topochemical Design Laboratory,
RIKEN Frontier Research System,
2-1 Hirosawa, Wako 351-0198

[3]Nanotechnology Research Center, Research Institute
for Electronic Science, Hokkaido University,
N12W6, Sapporo 060-0812

[4]Department of Integrated Sciences in Physics and Biology,
College of Humanities and Sciences, Nihon University,
3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156-8550

Received November 20, 2006; E-mail: shimo@poly.es.hokudai.ac.jp

A smooth TiO_2 hollow-spheres array, a kind of inverse opals, was prepared in a wide area ($>1 \times 5$ cm) in a short time (less than 1 min excluding sintering) using a spin-coating technique. A two-dimensional colloidal crystal was used as a template. The TiO_2 sintering process, especially the rate of the temperature increase, was important to copy the periodicity of the colloidal crystal structure. The electron diffraction image taken by the transmission electron microscopy observation showed that the hollow-spheres arrays have anatase-type crystal structure.

Self-assembled-type photonic crystals have been actively studied. The reasons might be: the photonic crystal is very interesting from theoretically and experimentally; self-assembled-type photonic crystals, especially the inverse opals,[1,2] can be prepared easily and inexpensively, and also easily chemically modified.[1,3–5] However, generally, the surfaces of the structures are relatively unsmooth. The unsmooth surface is undesirable from the viewpoint of the photonic crystal, because the unsmooth surface has less evanescent resonance.

As a method to prepare smooth surface, the layer-by-layer method,[6] especially the surface sol–gel method[7] is well-known. However, the surface sol–gel method takes a long preparation time to form the thicker walls. For instance, to prepare 20 nm layers, dipping must be done 60 times, i.e., more than five hours are necessary. Additionally, Fujikawa and Kunitake have reported that 20% of the structure collapses during the removal of the base particles.[8] In this paper, we report a spin-coating method to overcome those disadvantages.

Experimental

Particle Self-Assembly. An indium tin oxide substrate (1×5 cm, 10 Ω cm^{-2}) was dipped in 0.1 M NaOH aqueous solution for 30 min for hydrophilation. This hydrophilation was required for the two-dimensional particle self-assembly (described later). Polystyrene particles (0.596 ± 0.006 µm (refered as 0.6 µm), Nanosphere™ Size Standards, NIST Traceable Polystyrene Polymer, Polysciences, Inc.) were two-dimensionally (2D) crystallized on the substrate. The self-assembly technique for the preparation of 2D colloidal crystal was originally proposed by Denkov et al.[9] Due to water evaporation and capillary forces, the particles that are suspended in water form 2D crystals on the substrate. Details of the fabrication process have been reported elsewhere.[10] The particle suspension (≈0.5 mL) was injected into a hand-made glass cell. Then, the *x*-axis stage, on which the substrate was mounted, was translated continuously at a controlled rate. The particles were flowed gathered at the meniscus edge due to the capillary force, and formed particle layers on the glass substrate. By moving the substrate as the same speed with the particles flow, we could from particle layers.

The moving rates to prepare single particle layers were 2, 4, and 10 µm s^{-1} for 1.0, 0.6, and 0.4 µm diameter particles, respectively. The temperature was 21 °C, and the ambient humidity was 62–66%. The particle assembly process was observed using a CCD camera. Well-ordered 2D crystal with typical dimensions of 10×30 mm were prepared.

Prevention of Mechanical Peeling. The spin-coating process involves a horizontal centrifugal force on the sample surface. The resulting colloidal crystal was physically adsorbed on the glass substrate, and apt to be mechanically peeled off. To prevent the peeling, the thermal bonding between polystyrene particles was necessary in the case of the viscoelastic high-concentrated (over 10%) ethanol solution of titanium(IV) tetrabutoxide. The colloidal crystals were heated at 40 °C in 30 min in an incubator. The thermal polymer bonding formation had been elucidated theoretically and experimentally by other researchers.[11,12]

Spin-Coating. An ethanol solution (30 µL) of titanium(IV) tetrabutoxide (Wako Pure Chemical Industries, Ltd.) was deposited on the crystal by spin coating; the initial spinning rate was 500 revolutions per minute (rpm) during the first few seconds (2–20 s) before the higher rates (over 500 rpm) for stable rotation. Due to its high reactivity, the gelation time of titanium tetrabutoxide solution depended on the atmosphere and humidity. In our experimental setup, the temperature was fixed at 21 °C, and the ambient humidity was 62–66%. The concentration, revolution rates, and rotation times are summarized in Table 1.

Sintering. The spin-coated samples were sintered at 450 °C for 30 min in an electric oven. Titanium(IV) tetrabutoxide was dehydrated, and titanium dioxide (TiO_2) formed during the sintering process. The rate of temperature increase is also shown in Table 1.

Analysis. The resulting materials were observed by scanning electron microscopy (SEM, Hitachi S5200), transmission electron microscopy (TEM, JOEL JEM2100F), and optical microscopy

Table 1. Preparation Parameters of Smooth Hollow-Spheres Array

Concentration /%	Revolution rate/rpm	Rotation time/s	Rate of temperature increase/°C h^{-1}
2–50	300–1000	30–50	85–430

Published on the web June 13, 2007; doi:10.1246/bcsj.80.1226

(Olympus BX-50). The absorption spectra of the 2D crystal and the resulting materials were measured by microscopic spectroscopy technique combined with a high sensitivity spectrophotometer (Horiba Jobin Yvon TRIAX 320 and SPECTRUM-1).

Results and Discussion

Concentration of Titanium Ethanol Solution. The particle suspensions were attached on the substrate before the beginning of the two-dimensional crystallization, and isolated particles were adsorbed on the substrate. These isolated particles were utilized to find the best concentration ethanol solution of titanium to form the smooth surface.

The experimental parameters for the concentration change of titanium ethanol solution were as follows; the rate of revolution was 500 rpm for 20 s and then 1000 rpm for 30 s. The rate of temperature increase after the spin-coating process was $\approx 140\,^{\circ}\mathrm{C\,h^{-1}}$.

The SEM images of the isolated TiO_2 shells are shown in Supporting Information. The polystyrene spheres burned out during the sintering process. The original particle diameter was 0.596 µm; however, the drying and sintering process caused the diameter to shrink ≈510 nm (≈14% shrinkage).

The TiO_2 shell obtained from the low-concentration solution of titanium ethanol had a rather rough surface. For instance, in the case of 2% titanium butoxide solution, 20 nm nanocrystals formed hollow spheres, and several nanometers slits were observed between the nanocrystals. The high concentration solution gave a thick wall and a smooth surface. However, the higher concentration solution became more viscous. On the contrary, in the case of the spin-coating on the colloidal crystals, the viscous solution could not enter into the narrow spaces between the particles. The best concentration condition to prepare the dense and flat surfaces on the colloidal crystals was 10%. The surface roughness was less than 2 nm observed via SEM.

Spin-Coating Speed. The spin-coating speed was also examined. Smaller revolution rate gave thicker walls of the spheres, but the coating became irregular. Faster revolution rate gave a uniform coating, but thinner walls formed. The suitable condition to prepare our TiO_2 shell was at 500 rpm for 2 s following at 1000 rpm for 50 s.

Rate of Temperature Increase. The most effective parameter on the structural periodicity is the rate of temperature increase. Both the slow and the fast rate of temperature increase made the unit ellipsoidal (Figs. 1a and 1b). The results revealed that the balance between the coalescent rate of polystyrene particles and the sintered rate of metal butoxide is important to form a spherical unit.

Our polystyrene particle melted at 100 °C and completely combusted at 300 °C. The covered titanium tetrabutoxide underwent a sol–gel transition and became a titania amorphous gel at lower temperature, and the amorphous gel became anatase at around 450 °C. The slow rate of temperature increase caused the titanium butoxide to be sintered after the polystyrene deformation to elipsoids (Fig. 1a, schematic image). The anatase TiO_2 nano-crystals formed on the polystyrene elipsoids, and then consequently formed into hollow elipsoids (Fig. 1a). In the case of the fast rate of temperature increase, the titanium butoxide was simultaneously sintered with the polystyrene combustion (Fig. 1b, schematic image). Thus, loose hollow elipsoids formed as the same as the fast rate of temperature increase (Fig. 1b).

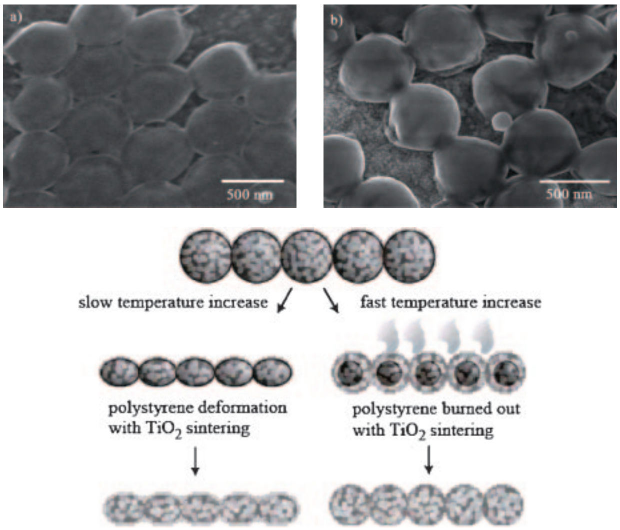

Fig. 1. SEM images of smooth hollow-sphere arrays (top view). Rate of temperature increase is $86\,^{\circ}\mathrm{C\,h^{-1}}$ (a) and $430\,^{\circ}\mathrm{C\,h^{-1}}$ (b). The schematic images of the influences of the rate of tempearture increase on the structures forming (cross section) are shown bottom.

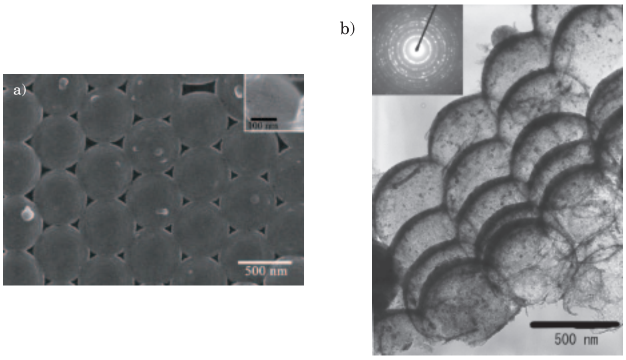

Fig. 2. SEM image (a) and TEM image (b) of ultra-smooth inverse opals. Rate of temperature increase was $143\,^{\circ}\mathrm{C\,h^{-1}}$. The electron diffraction is shown in inset (b).

Smooth Hollow-Spheres Arrays. The best balance of polystyrene deformation and titanium sintering gave us smooth spherical arrays (Fig. 2). 600 nm particles and 10 wt % titanium butoxide ethanol solution were used. The revolution rate was 500 rpm for 2 s, followed by 1000 rpm for 50 s. The best rate for the temperature increase under these conditions was $\approx 140\,^{\circ}\mathrm{C\,h^{-1}}$. The titanium-coating procedure took less than 3 min. This coating process time was about 0.001 times in comparison to the layer-by-layer method's. No structure collapsed during the removal of base particles. Basically, the spin-coating method overcomes the disadvantages of the layer-by-layer methods under the best conditions.

The SEM (Fig. 2a, inset) and TEM (Fig. 2b) images show the smooth spherical arrays were composed of several nanometer-sized crystals. The reflected optical microscopic image of the hollow-spherical monolayer showed a red color because

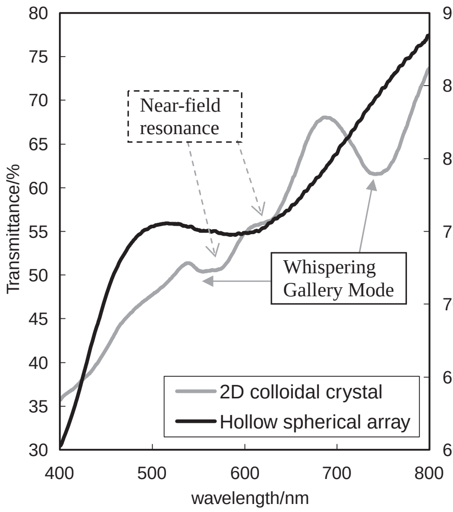

Fig. 3. Transmission Spectra of 600 nm particle colloidal crystal (gray line) and hollow-sphere array (black line).

of the high periodicity in the optical range (see Supporting Information). The analysis of the electron diffraction patterns (Fig. 2b, inset) revealed that they were TiO_2 anatase crystals, which is favorable as a photocatalyst.

Absorption Spectra. The absorption spectra of the 2D colloidal crystal of 0.6 µm polystyrene particles and the hollow-sphere array are shown in Fig. 3. The peaks in the range from 570 to 750 nm were not due to the Bragg diffraction; with a the 0.6 µm particle's periodicity, Bragg diffraction at the L-point should be observed around 1.4 µm.[13]

Miyazaki and Ohtaka have calculated of the particle-assembled-type photonic crystal.[14] The calculation for an isolated sphere of refractive index $n = 1.6$ with a diameter of 0.6 µm should show two marked whispering gallery (WG)-mode resonances of $l = 2$ and 3 at 742 nm (normalized frequency $\omega = (\sqrt{3}/2)(D/\lambda) = 0.7$) and 565 nm ($\omega = 0.92$), respectively. D is the lattice constant. From Fig. 3, we confirmed that the transmittance dips are related to the WG modes at 750 and 560 nm in the spectrum of the 2D colloidal crystal.

The transmittance of the TiO_2 hollow-spherical arrays was extremely low under 400 nm, because the titanium dioxide absorbs ultra-violet light (<380 nm) (Fig. 3). Let us discuss the another dip around 500–650 nm. Miyazaki's calculation uses polystyrene particles in air, and so, it cannot be applied to our titanium hollow-spherical arrays directly. However, the hollow-spherical array also had a periodic structure in the optical wavelength scale; thus, it should have the same optical phenomena with the 2D colloidal crystals. Generally, the WG mode is caused by a confined photon in a sphere, which is composed of a higher-refractive index material than the one of the ambient. Thus, normal inverse-opals, which has a lower refractive index than the ambient ones, do not have the WG modes. However, in our hollow spherical arrays, the titanium oxide "shell" might be able to confine a photon as a leaky WG modes in the sphere (as Fig. 2). Tentatively, we applied Miyazaki's calculation to the shrinked diameter, 0.51 µm.

If our hollow-spherical array had the leaky WG modes, the modes would be observed around at ≈630 nm ($\omega = 0.7$) and ≈400 nm ($\omega = 0.92$). There is a possibillity that the leaky WG mode was included on the broad dip in the range of 500–650 nm. Apart from these leaky WG modes, it was calculated that the near-field resonance between particles should be observed at 512 and 501 nm for 0.51 µm 2D array.[15] There is also a possibillity that the near-field resonance mode was included in the broad dip between 500 and 650 nm in the transmittance spectrum. The authors think that the smooth surface of our hollow-spherical array might cause those evanescent resonance modes.

Summary

We have reported a simple and rapid preparation method of smooth hollow-spherical arrays which can bring the evanescent wave resonance. The titanium-coating procedure took less than 3 min, and the surface roughness was less than 2 nm. The rate of temperature increase was important. This hollow-spherical array was composed of anatase-type TiO_2 crystals, which are attractive as a photocatalyst. The investigation to find the suitable conditions for the multilayers of colloidal crystals should be continued.

The authors thanks to Ms. H. Takemoto, Ms. Kaoru Ito, and Ms. Sayori Yagi for their valuable helps. This work is supported by the Ministry of Education, Culture, Sports, Science and Technology (417).

Supporting Information

SEM and optical images. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

References

1 S. I. Matsushita, T. Miwa, D. A. Tryk, A. Fujishima, *Langmuir* **1998**, *14*, 6441.

2 N. Tétreault, H. Míguez, G. A. Ozin, *Adv. Mater.* **2004**, *16*, 1471.

3 D. Wang, A. L. Rogach, F. Caruso, *Chem. Mater.* **2003**, *15*, 2724.

4 P. Lodahl, L. F. van Driel, I. S. Nikolaev, A. Irman, K. Overgaag, D. Vanmaekelbergh, W. L. Vos, *Nature* **2004**, *430*, 654.

5 A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti, V. G. Ralchenko, *Science* **1998**, *282*, 897.

6 Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, *Langmuir* **1996**, *12*, 3038.

7 I. Ichinose, T. Kunitake, *Chem. Rec.* **2002**, *2*, 339.

8 S. Fujikawa, T. Kunitake, *Langmuir* **2003**, *19*, 6545.

9 N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, K. Nagayama, *Nature* **1993**, *361*, 26.

10 S. I. Matsushita, T. Miwa, A. Fujishima, *Langmuir* **2001**, *17*, 988.

11 Z. Tadmor, C. G. Gogos, *Principles of Polymer Processing*, John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore, **1979**.

12 S. Matsuo, T. Fujine, K. Fukuda, S. Juodkazis, H. Misawa, *Appl. Phys. Lett.* **2003**, *82*, 4283.

13 S. I. Matsushita, M. Shimomura, *Chem. Commun.* **2004**, 506.

14 H. Miyazaki, K. Ohtaka, *Phys. Rev. B* **1998**, *58*, 6920.

15 H. T. Miyazaki, H. Miyazaki, K. Ohtaka, T. Sato, *J. Appl. Phys.* **2000**, *87*, 7152.