Preparation and Optical Properties of Spherical Inverse Opals by Liquid Phase Deposition Using Spherical Colloidal Crystals

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Abstract. Titanium dioxide (TiO$_2$) inverse opals in spherical shape were prepared by liquid phase deposition (LPD) using spherical colloidal crystals as templates. Spherical colloidal crystals were produced by ink-jet drying technique. Aqueous emulsion droplets that contain polystyrene latex particles were ejected into air and dried. Closely packed colloidal crystals with spherical shape were obtained. The obtained spherical colloidal crystals were used as templates for the LPD. The templates were dispersed in the deposition solution of the LPD, i.e. a mixed solution of ammonium hexafluorotitanate and boric acid and reacted for 4 h at 30 °C. After the LPD process, the interstitial spaces of the spherical colloidal crystals were completely filled with titanium oxide. Subsequent heat treatment resulted in removal of templates and spherical titanium dioxide inverse opals. The spherical shape of the template was retained. SEM observations indicated that the periodic ordered voids were surrounded by titanium dioxide. The optical reflectance spectra indicated that the optical properties of the spherical titanium dioxide inverse opals were due to Bragg diffractions from the ordered structure. Filling in the voids of the inverse opals with different solvents caused remarkable changes in the reflectance peak.

1. Introduction

The fabrication of three-dimensional (3D) ordered macroporous materials with pore sizes in the submicrometer range has been of considerable interest [1]. Such materials have great potential in a variety of areas, including photonics [2-4], catalysis [5] and separation media [6,7]. Of particular interest are dielectric 3D periodic structures. These 3D structure lead to a periodic modulation of the refractive index generating a photonic stop band that does not allow the propagation of light with a definite wavelength [8,9]. They exhibit remarkable optical properties and have great potential in a wide range of scientific and technical applications such as optical filters [10,11], optical switches [12], wave-guides [13], optical fibers [14], and miniaturized spectrometers [15]. A widely used approach to making 3D ordered macroporous materials is to fill the interstitial spaces of a colloidal template (synthetic opal) with the solid and subsequently to selectively remove the template materials [1]. A colloidal crystal template is usually prepared by self-assembly of mono-dispersed spherical particles in an opal structure. Infiltration methods include the sol-gel method, electrodeposition, suspensions of nanoparticles, and chemical vapor deposition (CVD). The subsequent removal of the template yields an inverse opal material with a close-packed arrangement of voids.
One of the important issues in the design of colloidal crystals and inverse opals are the control of their uniformity in size and shape [16]. Several research groups have reported some methods to fabricate colloidal crystals and inverse opals with spherical shape [16,17].

We have used liquid phase deposition (LPD) with a colloidal template to fabricate TiO$_2$ inverse opals [18]. The LPD method is a wet process to deposit metal oxide thin film. Metal oxide or hydroxide thin films form by means of a ligand-exchange (hydrolysis) equilibrium reaction of metal-fluoro complex species $MF_x$ and a consumption reaction with boric acid as the F$^-$ scavenger. This method enables the homogeneous metal oxide or hydroxide thin films to be formed on various substrates by simply immersing them in the reaction solution.

Here, we report a simple method to fabrication of spherical titanium dioxide inverse opals. The colloidal crystals with spherical shape were fabricated by the evaporation-induced crystallization of polystyrene (PS) latex suspension droplets that were generated by ink-jet technique. Next, the colloidal crystals were used as templates for the LPD. The interstitial spaces of the colloidal crystal were completely filled with titanium dioxide by the LPD process. Finally, PS latex particles were removed by calcination, which left macropores at their sites. The obtained TiO$_2$ inverse opals with spherical shape were in the range of few tens of micrometers in size. The ordered pore diameters were in the range of a few hundreds of nanometers and could be adjusted by using different size of PS latex particles. These TiO$_2$ inverse opals are of practical significance in wide areas of applications such as photonic crystals, photocatalysts and separation media.

2. Experimental

2.1. Preparation of PS colloidal crystals with spherical shape by ink-jet drying
The carboxylated PS latex colloidal particles were purchased from Sakuranomiya Chemical Co. Ltd. The average diameters of the particles was 255 nm. 13.6 wt% of PS latex suspension were ejected by ink-jet equipment (Cluster Technology, Pulse Injector PIJ-40, nozzle diameter 40 μm) into 80 °C heated air. Spherical PS colloidal crystals were generated by evaporation-induced self-assembly of polystyrene (PS) latex suspension droplets that were generated by ink-jet technique.

2.2. Preparation of TiO$_2$ inverse opals by the LPD
The parent solutions used for the LPD were aqueous solutions of (NH$_4$)$_2$TiF$_6$ and H$_3$BO$_3$. (NH$_4$)$_2$TiF$_6$ (Kishida Chemical Co. Ltd.) and H$_3$BO$_3$ (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$_4$)$_2$TiF$_6$ and 0.2 mol dm$^{-3}$ for H$_3$BO$_3$, and used for the deposition solution for the LPD method. The PS spherical colloidal crystals obtained were soaked in the deposition solution of the LPD, and kept for 4 h at 30 °C. The colloidal crystals were then separated from the solution, washed with distilled water, and dried at ambient temperature. The PS latex particles were removed by calcination in air. The temperature was increased at a rate of 0.5 °C min$^{-1}$ to 400 °C and stabilized at 400 °C for 1 h before being decreased to ambient temperature.

2.3. Characterization
The morphology and microstructure of the synthesized composites and inverse opals were observed by scanning electron microscopy (SEM, JEOL JSM-6301F) and transmission electron microscopy (TEM, JEOL JEM-2000EX). Prior to the SEM observation, the samples were sputter coated with Au. The X-ray diffraction measurements were performed on a Rigaku RINT-2500HFV using Cu Ka irradiation. The optical properties of samples were investigated by recording their transmission and reflection spectra using a Shimadzu UV-3600 spectrophotometer.

3. Results and Discussion
The PS particles inside the suspension droplets self-assembled into spherical colloidal crystals spontaneously when the aqueous solvent was removed from the droplets by evaporation. The capillary
force close-packes the PS particles into their final configuration, and van der Waals’ forces subsequently cement the PS particles together. Figure 1 shows the optical micrograph of the spherical colloidal crystals. The colors arise from light diffraction (opalescence) from the colloidal arrays. This is clear evidence of long-range ordering of the PS particles as shown in the SEM images of figure 2 for the internal arrangement of a colloidal crystal of PS particles. Figure 2 shows SEM images of the spherical colloidal crystals. The spherical colloidal crystals were ~30 μm in diameter and consist of closely packed PS particles in a face-centered cubic arrangement due to a relatively large capillary force at the air-water interface.

The optical reflectance spectrum of the spherical colloidal crystals is shown in figure 3. The reflection peak appears around 600 nm. Because the spherical surface of the colloidal crystal is the (111) plane of the fcc lattice, the angle between the incident beam and the surface is not the same over the surface of the colloidal crystal, resulting in a rather broad reflection band. The reflection peak is consistent with the estimates from Bragg’s law.

Next, the prepared spherical colloidal crystals were used as template materials for the LPD process. The prepared spherical colloidal crystals were soaked in a reaction solution of LPD process, which went through the interstices between PS latex particles by capillary force. Then titanium oxide deposited by means of hydrolysis reaction of (NH₄)₂TiF₆ on the template surface. After reaction for 4 h, the interstitial spaces of template were completely filled with titanium oxide. In the LPD process, titanium dioxide is deposited via heterogeneous nucleation. In this work, we have used carboxylated polystyrene particles as template. In this case, titanium oxide is preferentially deposited onto hydrophilic polystyrene surface and consequently deposition of free titanium oxide hardly takes place. The as-deposited sample was amorphous in X-ray diffraction, but Raman spectroscopy indicated that the infiltrated sample was anatase TiO₂. After a calcination at 400 °C for 1 h, the PS latex particles as template were removed, leaving ordered spherical air voids at their sites in the matrix of TiO₂. SEM images of the calcined sample are shown in figure 4. As shown in figure 4, spherical inverse opals were successfully produced. The void size was reduced to 214 nm due to the shrinkage during the calcination. Nevertheless, spherical shapes of colloidal crystals were kept, as shown from a low-magnification image of figure 4. No cracks were observed for the prepared spherical inverse opals, although some cracks due to shrinkage during the calcination were observed for inverse opals prepared by the LPD method onto the glass substrate [18].

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 TiO₂.
The optical reflectance spectrum of the TiO$_2$ spherical inverse opals is shown in figure 5 (a). The reflection peak appears around 430 nm, consistent with Bragg’s law. Filling in the voids of inverse opals with solvents caused a change in the average refractive index of the material. It also caused a change of position of the reflection peak [19]. To investigate the solvent-filling effects, we chose a group of solvents that spanned a range of refractive indices. The solvents were: air (n = 1.00), 1-pentanol (n = 1.42), and 1,2-dibromobuthane (n = 1.54). Figure 5 shows the optical reflectance spectra of TiO$_2$ spherical inverse opals filled with solvents. The absorption peaks assigned to the stop band shifted to higher wavelengths for higher refractive index solvents.

![Optical reflectance spectrum of TiO$_2$ spherical inverse opals filled with various solvents.](image)

**Figure 3.** Reflectance spectrum of spherical colloidal crystals formed by 255 nm PS latex particles.

**Figure 4.** SEM images of the spherical inverse opals. (a) Low-magnification image. (b) Surface image. (c) Fractional section image of broken inverse opals.

**Figure 5.** Reflectance spectra of spherical inverse opals filled with various solvents. (a) air, (b) 1-pentanol, and (c) 1,2-dibromobuthane.
4. Conclusions
Spherical PS colloidal crystals and spherical TiO$_2$ inverse opals were fabricated in this study. Spherical colloidal crystals were produced by ink-jet drying technique. The PS particles inside the suspension droplets self-assembled into spherical colloidal crystals spontaneously when the aqueous solvent was removed from the droplets by evaporation. TiO$_2$ spherical inverse opals were synthesized by using the LPD method using a spherical colloidal crystal as a template, followed by removing of the PS latex particles by the calcination. SEM observations indicated that spherical inverse opals were successfully produced. The optical reflectance spectra indicated that the optical properties of the spherical TiO$_2$ inverse opals were due to Bragg diffractions from the ordered structure. Filling in the voids of the inverse opals with different solvents caused remarkable changes in the reflectance peak.

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