

Fabrication technique for filling-factor tunable titanium dioxide colloidal crystal replicas

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Filling-factor tunable titanium dioxide replicas of colloidal crystals were fabricated by using a liquid phase deposition (LPD) technique. Ammonium hexafluorotitanate $[(\text{NH}_4)_2\text{TiF}_6]$ was used as a precursor, which was converted slowly to titanium dioxide by hydrolysis with boric acid. After the oxide was formed in voids of latex colloidal crystals, the latex was removed by calcination. By applying the LPD process to the replica again, the filling factor of the replica could be increased in a controllable fashion. With 203 nm template spheres, the peak shift in the ~ 490 nm stop band depended linearly on the deposition time for the first 20 min, at a rate of 4.4 nm/min. Thus the position of the Bragg reflection peak could be adjusted precisely by controlling the filling factor of the replica structure. © 2002 American Institute of Physics. [DOI: 10.1063/1.1524693]

In the years since the existence of the photonic band gap was predicted by Yablonovitch,¹ many efforts have been made to realize three-dimensional (3D) photonic crystals. Many applications have been proposed, including low threshold lasers,² waveguide structures that enables the light to curve at acute angles,³ and perfect dielectric mirrors.⁴

The assembly of colloidal crystals from nanosized spheres is one of the most promising approaches to the problem of fabricating 3D photonic crystals. Latex polymer and metal oxide spheres with diameters in the range of tens to thousands of nanometers can easily be crystallized into face-centered cubic (fcc) structures, and sophisticated techniques have been developed for making defect-free crystals of up to millimeter size.^{5–11} Although a complete photonic band gap in the visible region has never been achieved with colloidal crystals, because the dielectric contrast between two materials (spheres and voids) must be 2.8 or more,¹² stop bands (band gaps which open only in a certain crystal directions) have been widely reported. In general, stop bands arising from the (111) and (220) Bragg reflections of light have been observed with fcc colloidal crystals.^{13,14}

Colloidal crystals are fascinating and versatile materials for the study of the photonics because they can serve as templates for the synthesis of high contrast replica materials. In the fcc structure, spheres occupy 74% in volume of the unit cell and voids occupy the remaining 26%. Many materials can be infiltrated into the voids to change their optical, chemical, and physical properties. After filling the template with a second material or its precursor, a replica is produced by removing the template. In this case, it is possible to real-

ize a full photonic band gap if the filling material has a sufficiently high refractive index.¹⁰

The peak wavelength of a reflection from a colloidal crystal (or synthetic opal) and its replica (inverse opal) is determined by the diameter of the spheres and by the dielectric constants of the two media, the spheres, and the voids (or the void spaces and the framework, in the case of a replica material). Although the peak wavelength can be adjusted continuously by changing the diameter of the spheres, in practice this approach is unwieldy because not all sphere sizes are readily available. Another approach is to tune the dielectric properties of either the spheres or the framework. Typically, one desires a refractive index for the framework that is as high as possible because this leads to a more complete band gap. Titanium dioxide is one of the best available materials in this regard. It has a refractive index of 2.5 in anatase phase, 2.9 in rutile phase, and good transparency throughout the visible region of the spectrum.¹⁵

Several papers have reported replica structures made by hydrolysis or decomposition of titanium alkoxides.^{9,16,17} Titanium dioxide formed by the hydrolysis reaction is hydrated and amorphous, and thus its refractive index is lower than that of single crystalline titanium dioxide.¹⁸ Furthermore, the reaction involves volume shrinkage that can cause cracking of the colloidal crystal into small fragments. Disclinations along domain walls and cracks increase the scattering of light and lower the overall optical quality of the material. Recently, Schroden and coworkers have demonstrated that control of the particle size of infiltrated zirconium and titanium oxides grown from these precursors is essential to the creation of high quality photonic materials.¹⁸ Turner *et al.*¹⁹ also recently reported that high quality titanium dioxide inverse opals could be made from silica-sphere-titania com-

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posites, and that cracking could be avoided by using a polymer backing to support the material during template removal.

Recently, new techniques have been developed for growing metal oxide films from supersaturated solutions. These liquid phase deposition (LPD) techniques use fluorides such as ammonium hexafluorotitanate $[(\text{NH}_4)_2\text{TiF}_6]$ and titanium tetrafluoride (TiF_4) dissolved in acid aqueous solutions, and give thin films of crystalline anatase on many kind of substrates and particles.^{20–24} In this letter, we describe the adaptation of the LPD technique to the synthesis of anatase colloidal crystal replicas. We show that the film thickness control possible with this method allows one to tune the position of the stop bands precisely.

Monodisperse carboxylate modified polystyrene (CMPS) latex spheres were purchased as a suspension from Seradyn Co. and used without purification. The suspension was diluted with 18.3 M Ω cm deionized (DI) water to a concentration of 0.05 to 0.25 wt %. Colloidal crystals were prepared by a modification of the method of Jiang *et al.*¹⁴ After the colloidal suspension was dispersed ultrasonically in a glass vial for 30 min, a glass substrate was immersed vertically. The glass substrate had been cleaned ultrasonically with water and isopropanol, rinsed with water, and then dried in an air stream. The vial was kept in an oven at 55 °C for 1 to 2 days until the suspension was fully evaporated, leaving a colloidal crystal on the glass surface.

The colloidal crystals were then soaked in an aqueous solution of ammonium hexafluorotitanate $[(\text{NH}_4)_2\text{TiF}_6]$, 99.99%, Aldrich Co.] and boric acid (H_3BO_3 , 99.5%, Aldrich Co.). Uniform titanium dioxide films were grown from 0.1 to 0.3 M ammonium hexafluorotitanate and 0.2 to 0.5 M boric acid. The pH of the solution was adjusted to about 3 by adding hydrochloric acid. By holding the sample in the solution at 50–70 °C for 10–30 min, it was possible to fill the void volume of the template completely with the solid titanium dioxide precursor. No shrinkage was observed during the LPD process prior to calcination. The sample was rinsed with DI water and dried in air at room temperature. After the latex spheres were removed by calcination at 400 °C for 8 h, a highly ordered replica consisting of a titanium dioxide framework with air holes was obtained [Figs. 1(a) and 1(b)].

In order to adjust the thickness of the walls of the framework, the LPD process was applied to the replica again after the template spheres were removed, using the same solution composition as in the first filling cycle. After the second LPD step, the sample was again calcined at 400 °C for 8 h. The thickness of the framework walls could be controlled by adjusting the time of the second LPD step. For example, with a deposition time of 30 min at 65 °C, the reflection peak was shifted about 100 nm (Figs. 3 and 4).

Each step of the LPD replication technique can be monitored optically. Using Bragg's law for normal incidence as shown in Eq. (1), physical parameters such as the diameter of spheres and the refractive index of the framework can be estimated if the position of a reflection peak λ_p can be measured precisely:

$$\lambda_p = 2d \sqrt{n_s^2 f + n_v^2 (1-f)}. \quad (1)$$

Here, n_s is a refractive index of spheres or air hole and n_v is a refractive index of voids or framework. In case of the

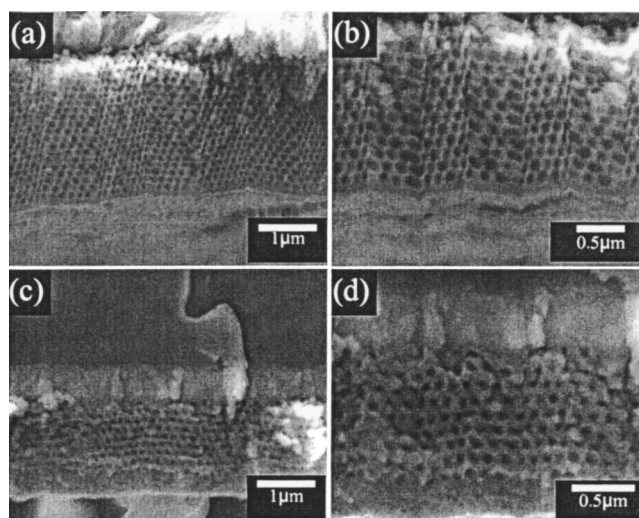


FIG. 1. (a) Scanning electron microscope image of a titanium dioxide replica after the first LPD deposition and calcination steps. Samples grown on glass substrates were fractured and then coated with Au by evaporation. (b) Enlargement of (a). (c) Replica after the second deposition and calcination. (d) Enlargement of (c). The film that appears on top of the colloidal crystal replica in (c) and (d) is a layer of nonporous TiO_2 from the second LPD process.

(111) reflection from a fcc structure, d is $0.8165D$, where D is a diameter of spheres, and f is the filling factor (0.74) for spheres. Figure 2 shows transmission spectra of colloidal crystals used as the template and just after the first and second LPD processes. The diameter of the template spheres can be calculated as 182 nm by Bragg's law from the measured reflection peak (436 nm, at the bottom of Fig. 4) and the refractive index of the spheres (polystyrene, $n = 1.6$). After the first LPD process and before calcination, the sample consists of CMPS spheres ($n = 1.6$, $D = 182$ nm) with 26 vol % titanium dioxide. Applying Bragg's law again, by using the measured peak position (532 nm in Fig. 2, middle), the refractive index of the deposited titanium dioxide was calculated as 2.25. Single crystalline anatase has a refractive index in the range of 2.4 to 2.5.¹⁶ The slightly lower value obtained here is indicative of partial hydration of the solid phase, as expected from an aqueous deposition process.

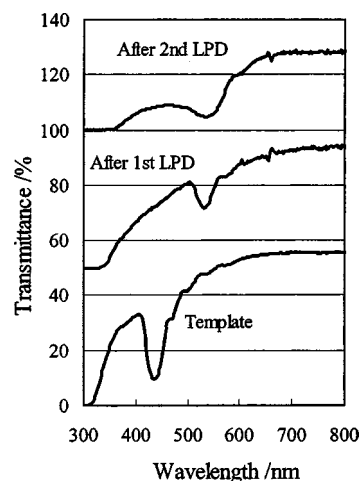


FIG. 2. Transmission UV-visible spectra of a template (182 nm in diameter), after the first deposition (65 °C, 15 min) and after the second deposition (65 °C, 30 min).

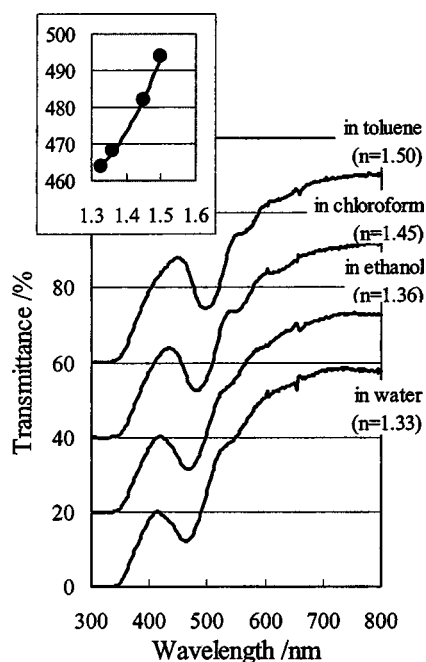


FIG. 3. Transmission UV-visible spectra of a sample after the first calcination. The sample was soaked in solvents with different refractive indices. The reflection peak maximum was shifted to 464, 468, 482, and 494 nm after soaking in water, ethanol, chloroform, and toluene, respectively. The diameter of air holes and the refractive index of framework were estimated as 169 nm and 2.40, respectively. (Inset: Reflection peak shift versus refractive index of solvent.)

In order to characterize the optical properties of the replica framework after the first calcination step, the sample was soaked in solvents with different refractive indices: water ($n=1.33$ at room temperature), ethanol ($n=1.36$), chloroform ($n=1.45$), and toluene ($n=1.50$). The spectra obtained under these conditions allow us to estimate both the diameter of the air holes and the refractive index of titanium dioxide framework simultaneously. Using the reflection peak maxima shown in Fig. 3, the diameter of the air holes and the refractive index of the titanium dioxide framework were estimated as 169 nm and 2.40, respectively, by using the quasi-Newton method to solve the simultaneous Bragg equations. The reduction of the diameter (shrinkage) and the increase of the refractive index to that of crystalline anatase are consistent with the loss of water of hydration upon calcination.

In order to estimate the filling factor and the refractive index of the replica after the second LPD process, we assumed that the interlayer space did not change during the process (i.e., $D=169$ nm before and after). Using peak maxima, the filling factor and the refractive index were again estimated. This calculation gave a volume fraction of 43% for the air holes and a refractive index of 2.43 for the framework. The diameter of air hole with a filling factor of 43% corresponds with about 80%–85% of that with a filling factor of 74%. This change could also be seen in the SEM images (Fig. 1). Within experimental error, the SEM images showed no change in lattice spacing during the second calcination step, consistent with the calculations from optical spectra. It is apparent from the SEM images that a layer of nonporous TiO_2 grows on top of the porous replica in the second LPD step. This dense layer may prevent complete filling of the lattice with TiO_2 .

The dependence of the reflection peak shift on the duration of the second LPD step was also determined. During the first 20 min, the peak shift increased linearly with deposition time (4.4 nm/min). The practical consequence of this observation is that the position of the stop band can be tuned precisely and continuously. After 20 min, the reflection peak maximum changed much more slowly (0.2 nm/min). This result suggests that the deposition process inside replica was essentially complete after 20 min.

In summary, we have found that the liquid phase deposition process is a convenient method for continuously adjusting the position of the stop band in titanium dioxide colloidal crystal replicas. Because the deposition occurs under mild conditions and gives conformal hydrous anatase films, it may be of general utility in synthesizing photonic materials with desired structures and properties.

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