Mesoscopic Photonic Crystals Made of TiO_2 Hollow Spheres Connected by Cylindrical Tubes

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The face-centered cubic (fcc) photonic crystals of titanium dioxide (TiO_2) hollow spheres connected by TiO_2 cylindrical tubes have been fabricated using silica template. The preparation process is based on the vertical deposition method, thermal sintering and selective etching techniques. In the crystal, the lowest energy pseudogaps at points U and K of the Brillouin zone have been opened.

Since 1987,[1,2] there has been growing interest in the fabrication of photonic crystals which are periodic arrangements on the optical wavelength scale.[3] The periodicity of the material modifies wave propagation, which can even be totally forbidden in certain frequency ranges. Because of their wide applications in optical technologies and telecommunications,[4,5] more and more various structures of three-dimensional photonic crystals have been exploited[6–9] in the last 15 years.

Using the colloidal crystals as template, some inverted opal structures have been fabricated.[10–16] Because the resulting of inverse opal structures may have a complete photonic bandgap,[17,18] these materials may have serious implications for modern photonics. However, the inverse opal is not the best topology in what it concerns optical gaps. The omnidirectional gap of inverse structures appears only for extremely high contrasts of the refractive index. The gap is not very large, and it is placed at high frequency values. Therefore, it would be desirable to find alternative colloidal crystal-based structures with better optical performances. Recently, Fujikawa et al.[19] have fabricated a three-dimensional structure of hollow titania spheres connected by cylindrical tubes. Maldovan et al.[20] have shown a rich variety of topologies with full gap performance.

In this letter, we report a kind of nonclose-packed (ncp) fcc photonic crystals of TiO_2 spherical shells connected by cylindrical tubes. With the help of thermal sintering, selective etching techniques, and sol–gel process, the fcc photonic crystals made of crystalline TiO_2 is fabricated using ncp silica opals as the templates.

The colloidal crystals of silica microspheres were firstly prepared on a silicon substrate by a modified vertical deposition method:[21] The silicon substrate covered with a glass microslide, which was treated with the hydrophobic water solvent, was vertically put into the ethanolic dispersion of the silica spheres with 534-nm diameter. After the ethanol was evaporated for 5 days, the film of silica opal with a certain thickness was deposited on the silicon substrate. Secondly, the obtained silica opal was sintered at 1010 °C for 3 h and the silica spheres in it would overlap each other. Then, the sintered opal was immersed in 1.0 wt % HF acid solution for 5–15 min and the ncp silica opals were formed. Finally, the ncp silica opal was used as the template to fabricate the ncp face-centered cubic structure by a sol–gel process. In the structure, each TiO_2 hollow sphere at the fcc lattice sites is connected to all of its 12 neighbors by 12 TiO_2 cylindrical tubes. First, the sol was prepared by mixing titanium tetraisopropoxide, anhydrous ethanol, deionized water, and diethanolamine with a certain molar ratio. Then, the ncp silica template adhered to a substrate was immersed in the sol for 5 min and sintered at 520 °C after pulling out from the sol. The cycle of dipping and sintering was repeated several times. Finally, the silica–titania composite was immersed in 20% aqueous NaOH solution for 48 h to remove the silica template.

Figure 1a shows the SEM surface image of the as-grown silica colloidal crystal. The dimension of the crystal on the substrate is approximately $8 \times 18\,mm^2$. It is clearly seen that the opal is a close-packed structure and the silica microspheres in it are not overlapped each other. So the thermal sintering technology[22] was applied to obtain the opals with a strong sphere overlapping (Figure 1b). After sintering, the shape of silica particles becomes nonspherical slightly and in close contact with each other. Figure 1c displays the SEM surface image of (111) face of an opal structure after etching for 15 min. In this structure, the spheres are not in contact any more but bridged by cylinders. As a consequence of the uniform etching process, a ncp face-centered cubic array of silica spheres connected by cylinders was formed.

Figure 2 shows the SEM images of the TiO_2 hollow sphere structure in different states of the ncp photonic crystals. Figure 2a corresponds to a (111) face of the silica–titania composite, from the picture it can be seen that the TiO_2 gelatin was not distributed into all the interspace among the silica spheres but was coated on the surface of the silica spheres and cylinders, and the thickness of the TiO_2 coating on the tubes is equal to that of on the spheres. As shown in Figures 2b and 2c, after the silica template was removed the hollow TiO_2 spheres are connected by the TiO_2 tubes and exhibit a ncp structure of the hollow sphere. We can see that although we replicate the fcc symmetry of the opal template, the

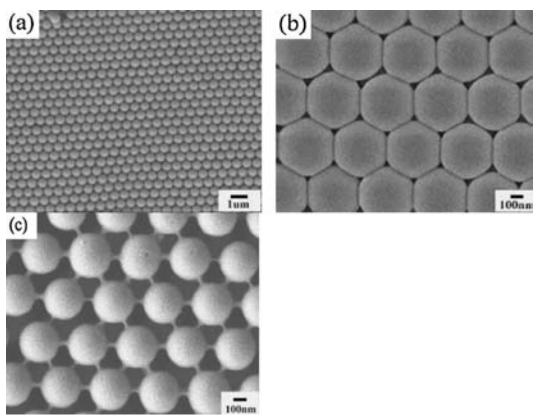

Figure 1. SEM images of planarized colloidal crystals made of silica microspheres of 534-nm diameter: a) As-grown colloidal crystal, b) after sintered at 1010 °C for 3 h, and c) ncp structure obtained after etching 15 min by HF acid.

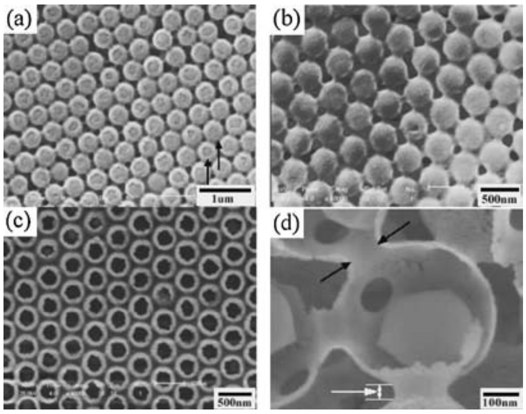

Figure 2. SEM images showing the TiO_2 hollow structures: a) Core–shell structure of silica–titania crystal (arrows indicated the TiO_2 coating), b) An array of TiO_2 hollow spheres at the upper surface of structure after removal of the silica template, c) A cross-section of (111) sphere layer in the array, indicating the homogeneous thickness of the shell, d) High-magnification showing the connectivity of the TiO_2 shells achieved.

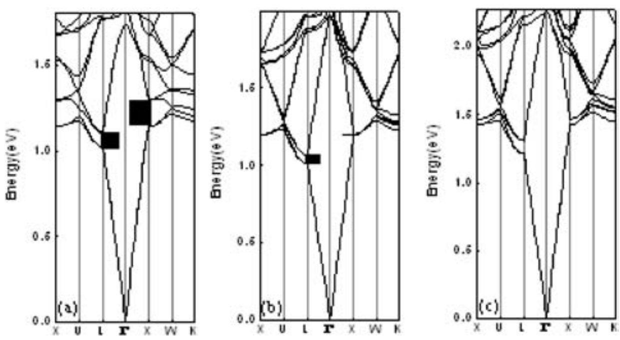

Figure 3. Photonic band diagram: a) Ncp structure of TiO_2 hollow spheres as described in text, b) As-grown SiO_2 opal, c) Ncp SiO_2 opal.

ncp crystals of TiO_2 hollow spheres are different to the inverted TiO_2 opals.[10] In the latter, the quasi-spherical air are connected through windows resulting from the direct replica of the original opal template, but in the former the spherical shells, the air spheres inside the shells and the air background outside the shells each connect to generate a multiply connected dielectric network. Figure 2d depicts a high-magnification SEM image of the channels bridging spherical shells. It is evident that the cylinders are hollow (indicated by black arrows) and have a certain length (indicated by white arrow). The result of X-ray diffraction shows that the crystalline phase of the TiO_2 is anatase. (here, the data are not given.)

Figure 3a shows the photonic band diagram of the ncp structure of TiO_2 hollow spheres described above (here, the centric distance between two neighbor spheres, the inside diameter of the spherical shells, the inside diameter of cylindrical tubes and the thickness of the TiO_2 shells are 482, 396, 46, and 32 nm, respectively. The dielectric contrast is taken as 7.84 in the calculations.). Compared with the fcc close-packed systems of SiO_2 microspheres (Figure 3b), the most important conclusion we can obtain is the larger values for the pseudogaps at low energies of the ncp structure of TiO_2 hollow spheres, not only around point L but also around point X of the Brillouin zone, and pseudogaps at point X become much larger than that at point L. Moreover, the pseudogaps at points U and K have been opened, and the band at point W also shows a more pronounced tendency to separate each other than bands of close-packed and ncp opal (Figure 3c) systems do.

In summary, using a colloidal crystal template of silica microspheres, we have successfully fabricated the ncp face-centered cubic structure of TiO_2 hollow spheres, in which, each hollow TiO_2 sphere connected with the nearest twelve hollow spheres by twelve cylindrical TiO_2 tubers. The band-structure calculations show the potential of the ncp lattices of hollow dielectric microspheres in terms of photonic bandgap properties.

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