# Characteristic of high-organized PS/BPS photonic crystals

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$B_2O_3$-$P_2O_5$-$SiO_2$ (BPS) three-dimensional (3D) high-organized polystyrene (PS) opals and inverse opals with large domain were fabricated and characterized. Scanning electron microscope (SEM) shows three or four small "windows", indicating that a very well interconnection between PS spheres of opal. The ultraviolet-visible (UV-vis) spectra indicate that the photonic band gaps (PBGs) are about 710 and 604 nm for 320- and 270-nm spheres respectively. While according to Bragg's equation, the simulation results should be 762 and 643 nm, which mean that 52 and 39 nm were shifted to blue region, respectively.

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Photonic crystals have received much attention as a medium for electronic and optical devices in the next generation. The photonic crystal is the periodic structures having lattice constants commensurate with wavelengths of visible and infrared photons[1,2]. Multiple interference of wave scattered from "atoms" in the lattice results in frequency range over which propagation of light is prohibited[3]. Hence this structure has a so-called photonic band gap (PBG) in which the presence of the optical field is forbidden[4].

In order to realize a PBG structure, a three-dimensional (3D) periodic structure is needed. Self-assembly of mono-dispersed spherical colloids into highly ordered lattices has attracted considerable attention due to the potential use of these periodic structures as photonic crystals (PCs)[5,6]. To fabricate high quality colloidal crystal films efficiently, a number of methods that take advantage of the forces of electric field[7,8], the flow of gas or liquid[9,10], and capillary force have been developed to assemble the particles to form uniform colloidal crystal films[11]. Among these, the gravity sedimentation method is the simplest way.

This letter reports that 3D high-organized polystyrene (PS) opals and $B_2O_3$-$P_2O_5$-$SiO_2$ (BPS) inverse opals with large domains were fabricated and characterized. Scanning electron microscope (SEM) shows three or four small "windows", indicating a very well interconnection between PS spheres of opal. The peak value indicates that the PBG was shifted to blue region.

Mon-dispersed PS spheres with an average diameter of 320 and 270 nm were purchased from Bangs Lab (USA). Silicon substrates were purchased from Electronic Tech. Group, 14th Institute (Tianjin). SEM experiments were carried out using ZEISS-SUPRA55. Transmission spectra were obtained using a Shimadzu UV-2501PC. Assembly opals were prepared by the gravity sedimentation and capillary forces on the leaning substrate. Inverse opals were prepared by infiltrating BPS sol-gel precursors into the interconnected nanometer periodic array of voids in the PS opals and subsequently removing PS spheres by heating at 500 °C for 1 h.

Figure 1 shows the (100) and (110) interface of highly ordered opal films with large domain size. The highly ordered hexagonal array indicates the (111) plane of the FCC lattice. Inverse opals with three (Fig. 2(a)) or four (Fig. 2(b)) small "windows" indicate that the holes connect the pores very well and the three or four "windows" pattern below each hole of the first layer indicate that the PS spheres are connected closely before infiltrating. Along the (111) and (100) direction, each sphere of air rests on the other three or four neighbors respectively. This observation of a regular cross pattern strongly confirms the perfect 3D structure in this zone of the film.

As we know, in the heating process, the PS spheres will be contracted. This contraction will cause the PS sphere diameter decrease. Here the diameter equals the distance between parallel lattices plane $d_{\mathrm{hkl}}$. On the other hand, the volume fraction of PS spheres ($f$) will be decreased too. This decrease will cause the average refraction index $n_{\mathrm{eff}}$ ($n_{\mathrm{eff}}^2 = f n_{\mathrm{block}}^2 + (1-f) n_{\mathrm{void}}^2$) increase. Here $n_{\mathrm{block}}$ and $n_{\mathrm{void}}$ are the refraction index of PS ball and the void. Before heating, based on Bragg diffraction equation ($\lambda_{\max} = 2n_{\mathrm{eff}} \cdot d_{\mathrm{hkl}} \cdot \sin\theta$), both the

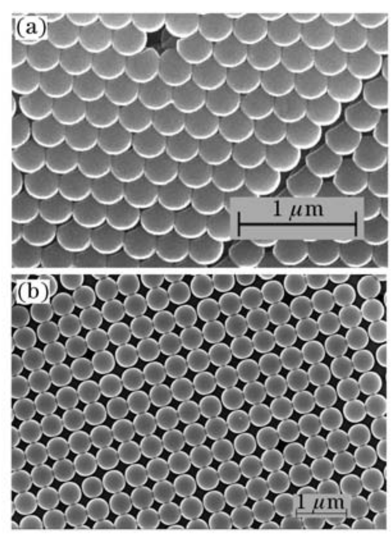


Fig. 1. SEM images of BPS inverse opals of (a) (100)-orientation regions and (b) (110)-orientation regions.

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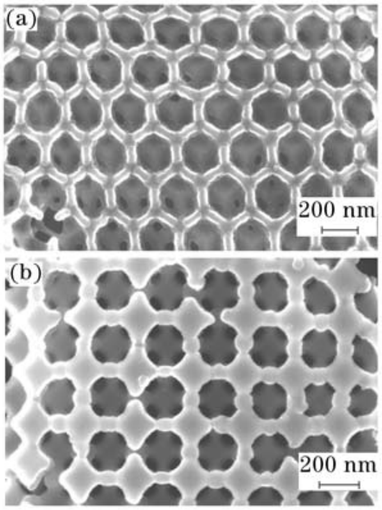


Fig. 2. SEM images of BPS inverse opals of (a) (111)-orientation regions and (b) (100)-orientation regions.

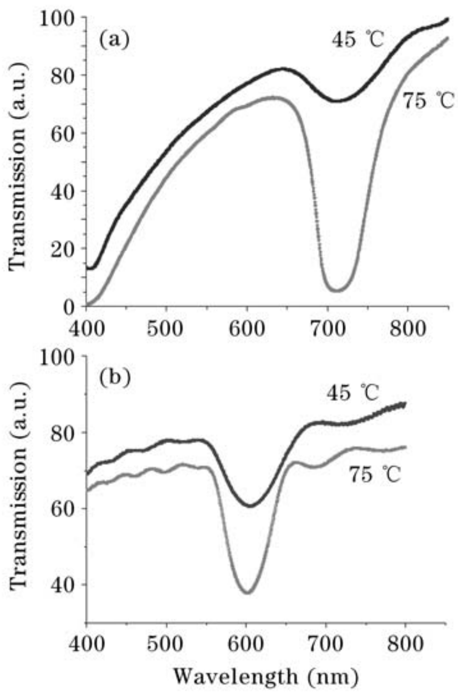


Fig. 3. UV-vis spectra of PS spheres of (a) 320- and (b) 270-nm diameters.

$n_{\text{eff}}$ and $d_{\text{hkl}}$ change will cause the change of wavelength $\lambda_{\max}$. The contraction will affect the $d_{\text{hkl}}$ more seriously than $n_{\text{eff}}$. Figure 3 shows the ultraviolet visible (UV-vis) spectra of an opal array that were assembled from 320- and 270-nm PS spheres respectively. The first-order diffraction peaks are about 710 and 604 nm. Based on Bragg diffraction equation, the peak values should be 762 (for 320 nm spheres) and 643 nm (for 270 nm spheres) before heating. It means the heating process might cause the PBG peak shift to blue region seriously.

In conclusion, highly organized 3D PS opals and inverse opals with very well connection were obtained. PBG region is seriously blue-shifted for the heating contraction.

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## References

1. B. Li, J. Zhou, Z. Yue, Z. Ma, Z. Gui, and L. Li, J. Inorg. Mater. (in Chinese) **15,** 977 (2000).
2. Z.-Z. Gu, S. Hayami, S. Kubo, Q.-B. Meng, Y. Einaga, D. A. Tryk, A. Fujishima, and O. Sato, J. Am. Chem. Soc. **123,** 175 (2001).
3. E. Yablonovitch, Phys. Rev. Lett. **58,** 2059 (1987).
4. S. John, Phys. Rev. Lett. **58,** 2486 (1987).
5. D. Wang, R. A. Caruso, and F. Caruso, Chem. Mater. **13,** 364 (2001).
6. W. Lee, S. A. Pruzinsky, and P. V. Braun, Adv. Mater. **14,** 271 (2002).
7. M. Holgado, F. Garcíia-Santamaría, A. Blanco, M. Ibisate, A. Cintas, H. Míguez, C. J. Serna, C. Molpeceres, J. Requena, A. Mifsud, F. Meseguer, and C. López, Langmuir **15,** 4701 (1999).
8. W. Wen, N. Wang, H. Ma, Z. Lin, W. Y. Tam, C. Chan, and P. Sheng, Phys. Rev. Lett. **82,** 4248 (1999).
9. S. H. Park and Y. Xia, Langmuir **15,** 266 (1999).
10. Z.-Z. Gu, Q.-B. Meng, S. Hayami, A. Fujishima, and O. Sato, J. Appl. Phys. **90,** 2042 (2001).
11. R. Mayoral, J. Requena, J. S. Moya, C. López, A. Cintas, H. Míguez, F. Meseguer, L. Vázquez, M. Holgado, and Á. Blanco, Adv. Mater. **9,** 257 (1997).