

Optical study of photonic crystal films made of polystyrene microspheres

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DOI: 10.1016/j.mencom.2007.01.002

An optical study of photonic crystal films made of monodisperse polystyrene microspheres is reported.

Photonic crystals (PCs) have become a fascinating field for physicists, materials scientists and optical engineers.^{1–3} The interest in PCs was induced by promising applications, such as low-threshold lasers, high-efficient light emitting diodes, perfect dielectric mirrors, planar waveguides, *etc.*⁴ The major physical property of PCs is the existence of photonic bandgaps in their photonic band structures. Depending on the structure of a PC and its refractive index contrast, the propagation of light within the PC can be prohibited either in all or in defined directions; this corresponds to the cases of full photonic bandgaps and stop-bands, respectively.^{5,6}

The self-assembly of monodisperse colloidal microspheres provides a suitable platform for the preparation of three-dimensional PCs. Ordered packings of submicron microspheres, also referred to as colloidal crystals or artificial opals, are widely used as model objects for the study of PC optical properties,^{7–12} as well as templates for the fabrication of inverse opals based on materials with a high refractive index.^{13–17} To date, a number of techniques have been developed for the preparation of high-quality colloidal crystals, such as natural sedimentation,^{7–11} centrifugation,¹⁸ spin coating,¹⁹ electrophoretic deposition,²⁰ vertical deposition,²¹ self-assembly in capillaries¹³ and confinement cells.²² The vertical deposition method stands out among others, since it allows rapid synthesis of PCs in a form of large-area thin films of controlled thickness.

Here we report an optical study of PC films prepared by the vertical deposition method. The correlation between structural and optical properties of PCs, as well as interpretation of experimental results using a simple diffraction theory, is discussed.

Monodisperse polystyrene microspheres with an average diameter of 655 nm and relative standard deviation less than 5% were synthesised by emulsifier-free emulsion polymerization of styrene using potassium persulfate as an initiator.²³ The mean diameter and size distribution were obtained from scanning electron microscopy (SEM), (LEO Supra VP 50 instrument) and dynamic light scattering (DLS, ALV CGS-6010 instrument and a 632.8 nm helium–neon laser as the light source) measurements. Colloids were centrifuged and re-dispersed in distilled water by ultrasonication. Glass microslides were thoroughly cleaned and immersed in ~1 vol.% aqueous suspension of microspheres. The temperature used for film growth was 45±1 °C. The samples were left undisturbed until the growth of films was completed. Finally, colloidal crystal films were annealed at 110 °C for 10 min to improve their mechanical stability.

Figure 1 shows typical SEM images of the top surface of a PC film, demonstrating the close-packed arrangement of polystyrene microspheres. Cross-section SEM images (not shown) reveal that colloids self-assembled onto a vertical substrate have a face-centered cubic (fcc) structure. Thus, hexagonally arranged microspheres observed in SEM images represent the (111) crystallographic plane. At a low resolution, the structure of the film can be considered as made of domains (up to 2000 μm² in size) of close-packed colloids, separated by domain boundaries [Figure 1(a)]. Depending on its size, each domain possesses a few or no point defects (usually, vacancies). These typical defects (namely, vacancy and domain boundary) can be better seen in a high-resolution SEM image [Figure 1(b)]. Nevertheless, it is worth noting that different domains have the same crystallographic orientation. This long-range order in the close-packed arrangement of microspheres was confirmed by two-dimensional Fourier transform of Figure 1(a) (inset).

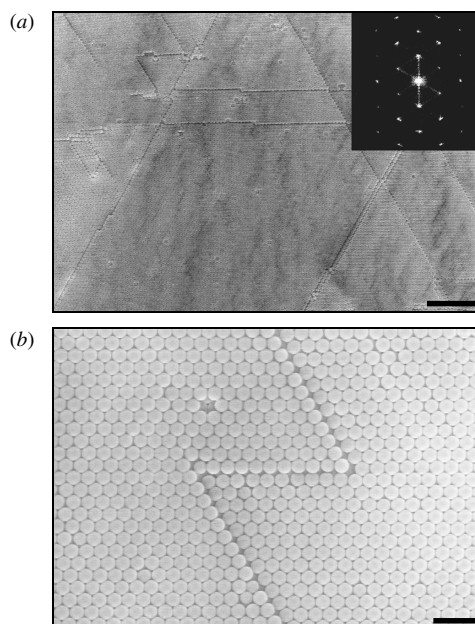


Figure 1 SEM images of a PC film made of 655 nm polystyrene microspheres. (a) Low-magnification image. The Fourier transform of the image is shown in the inset. Scale bar is 10 μm. (b) High-magnification image demonstrates the defects typically observed in a microsphere arrangement: vacancy and domain boundary. Scale bar is 2 μm.

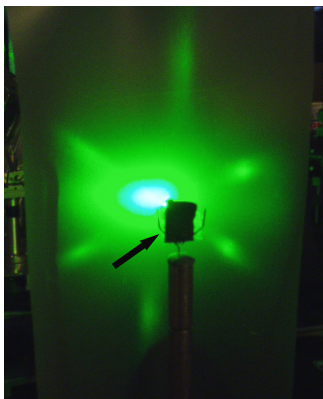


Figure 2 Optical photograph of a laser diffraction experiment. The sample is indicated by the arrow.

In order to verify the ordering of microspheres on a millimetre scale, an experiment on laser diffraction was carried out. Laser diffraction patterns were obtained using a beam with a 7 mm² cross section from a frequency doubled Nd:YAG laser ($\lambda = 532$ nm). Sixfold bright spot patterns indicate that the crystallographic orientation is preserved on a macro scale and defined by the direction of film growth (Figure 2). Thus, using a light beam of 0.2 mm² in diameter for transmission spectra recording, we assumed dealing with an ‘effective single crystal’ area of a PC film with all domains having the same orientation.

Optical transmission spectra were measured in the wavelength range 400–2000 nm using a double beam UV-VIS-NIR spectrophotometer (Varian Cary 500). The transmission spectrum in the direction normal to the PC film surface is shown in Figure 3. The arrows indicate the Fabry–Pérot oscillations, which occur due to the interference of light reflected from the top and bottom surfaces of the PC film. The presence of Fabry–Pérot fringes bears the witness of the constant thickness of the PC film within the illuminated area.^{12,21} The spectrum represents several pronounced drops in transmission; the nature of each minimum can be explained using the Bragg law for normal incidence

$$\lambda = \frac{2d_{(hkl)}}{k} n_{\text{eff}} \cos \theta_{(hkl)}, \quad (1)$$

where $d_{(hkl)}$ is the interplanar spacing for (hkl) crystallographic planes, k is the order of diffraction ($k = 1, 2, 3, \dots$), λ is the wavelength of radiation in a vacuum, and n_{eff} is the effective (average) refractive index of the polystyrene–air medium and $\theta_{(hkl)}$ is the angle between the light and the normal to the (hkl) planes. The effective refractive index can also be expressed as

$$n_{\text{eff}} = n_{\text{PS}} f_{\text{PS}} + n_{\text{air}} (1 - f_{\text{PS}}), \quad (2)$$

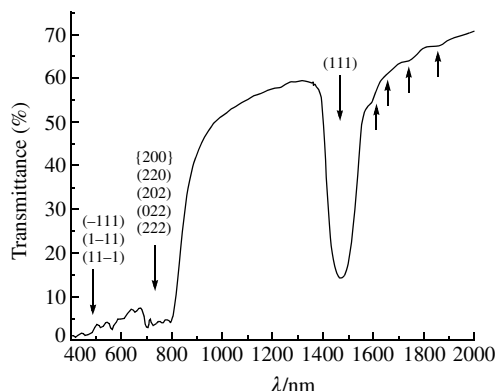


Figure 3 Transmission spectrum of a PC film in the $\langle 111 \rangle$ direction. The arrows indicate Fabry–Pérot fringes.

where n_{air} and n_{PS} are the refractive indices of air and polystyrene, respectively, and f_{PS} is the volume fraction occupied by polystyrene spheres in the PC film. Since $n_{\text{air}} \approx 1$, $n_{\text{PS}} \approx 1.5$ and for an ideal close-packed structure $f_{\text{PS}} \approx 0.74$, we can estimate n_{eff} to be 1.37.

Obviously, for PC with fcc symmetry only $\{111\}$, $\{200\}$ and $\{220\}$ plane families are essential for the interpretation of low-energy stop bands. First, we assume (111) planes to be parallel to the PC film surface, and the $\langle 111 \rangle$ direction to be that of light propagation. Having for (111) planes $d_{(111)} = a(2/3)^{1/2}$, where $a = 655$ nm is the average diameter of microspheres, and $\theta_{(111)} = 0^\circ$, we can predict the existence of minima in a transmission spectrum at 1464 and 732 nm, corresponding to the first ($k = 1$) and second-order ($k = 2$) diffractions, respectively [note that second-order diffraction on (111) planes can also be termed as diffraction on (222) planes]. Similarly, for (-111) , $(1-11)$ and $(11-1)$ planes, we have the same interplanar spacing $d = a(2/3)^{1/2}$, and $\theta = 70.53^\circ$, resulting in a first-order diffraction at 488 nm. In case of $\{200\}$ planes, $d_{\{200\}} = a/2^{1/2}$, and $\theta_{\{200\}} = 54.74^\circ$, resulting in a first-order diffraction at 732 nm. Finally, for (220) , (020) and (022) planes [we do not consider (-220) , (-202) and $(0-22)$ since they are parallel to the $\langle 111 \rangle$ direction of light propagation] we have $d = a/2$ and $\theta = 35.26^\circ$, resulting in a first-order diffraction at 732 nm. One can see that all calculated positions of diffraction wavelengths are in a good agreement with transmission minima observed in the experimental spectrum (Figure 3). Thus, such simple calculations can be used for the interpretation of the optical transmission spectrum in the direction normal to the PC surface. Note that different crystallographic planes make different contributions to the whole transmission spectrum, since they have different diffraction efficiencies.²⁴

As can be seen, the transmission minima at 488 and 732 nm resulted from the coincidence of diffraction peaks from different crystallographic planes. When tilting the angle of incidence, the combined peaks are splitting. Since these changes in positions of diffraction minima undergo in the visible region of spectrum, the samples possess strong iridescence and demonstrate all rainbow colours, when varying the observation angle [Figure 4(a)]. On the other hand, the splitting of diffraction peaks at 488 and 732 nm makes the interpretation of angle-dependent transmission spectra rather complex. For this reason, the angular dependence of transmission is shown for the first stop band at 1464 nm only [Figure 4(b)], for which the position of diffraction peak shifts to shorter wavelengths with the incidence angle obeying the Bragg–Snell law:

$$\lambda = 2d_{(111)} \sqrt{n_{\text{eff}}^2 - \sin^2 \theta_{(111)}}, \quad (3)$$

where all symbols are the same as in equation (1). The effective refractive index n_{eff} and interplanar spacing $d_{(111)}$ can be determined from the λ^2 vs. $\sin^2 \theta$ plot, because a linear fit to the experimental data has a gradient of $-4d_{(111)}^2$ and an intercept equal to $4d_{(111)}^2 n_{\text{eff}}^2$ (Figure 5). We found n_{eff} equal to 1.37, which exactly matches the value calculated using equation (2). Since the value obtained for $d_{(111)}$ is 532 nm, we can calculate the average diameter of polystyrene microspheres equal to 652 nm, which is in a good agreement with the results of SEM observations.

Thus, we reported the optical study of PC films prepared by the vertical deposition method. The crystalline quality of PCs was verified by laser diffraction; optical transmission measurements were carried out revealing stop bands in the $\langle 111 \rangle$ direction and allowing the estimation of the effective refractive index and lattice period of PCs. The features of optical spectra of PCs were interpreted using the basics of diffraction theory; the agreement between calculated and experimental results was noticeably good. Note that PCs made of polystyrene micro-

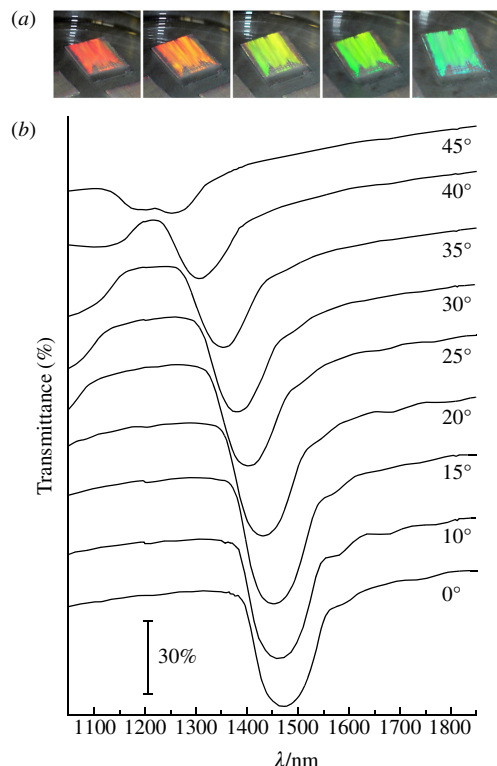


Figure 4 Angle-dependent optical properties of PC films. (a) Optical photographs of a PC film demonstrate the change in the iridescent colour, when tilting the angle of observation from glancing to normal. The symmetrical imprints in the bottom of film were left by the sample holder. (b) Transmission spectra of titania PC films measured at different angles of incidence θ . Spectra have the same coordinate range and were shifted vertically for the sake of clarity.

spheres of about 650 nm possess a photonic bandgap around 1.5 μm , while this wavelength region is of great importance for modern telecommunication technologies. These films can also be used either as templates for the preparation of inverse opals based on high-refractive-index materials^{13–17} or as host matrices for luminescent compounds,²⁵ liquid crystals²⁶ and non-linear media.²⁷

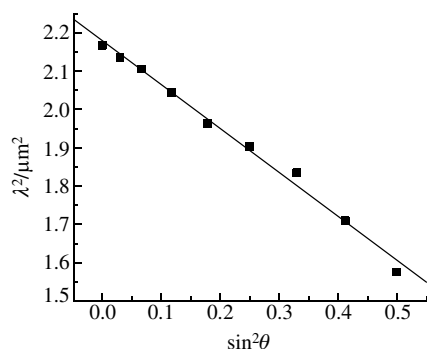


Figure 5 Plot of λ^2 vs. $\sin^2\theta$ (where λ is the wavelength of the minimum of transmission and θ is the angle of incidence) and the linear fit to the experimental data.

This work was supported by the Russian Foundation for Basic Research (grant nos. 05-03-32778 and 04-03-39010), the Programme for Fundamental Research of the Russian Academy of Sciences, the Federal Programme ‘Leading Scientific Schools’ (grant no. 2006.4568.2), and the Federal Target Science and Engineering Programme (grant no. 02.434.11.2009). We are grateful to Dr. A. G. Veresov for the SEM study of samples.

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Received: 18th September 2006; Com. 06/2782