Optical Properties of Colloidal Crystalline Arrays Composed of Hollow Polystyrene Spheres

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ABSTRACT: We have evaluated the optical properties of close-packed and non close-packed colloidal crystalline arrays made of hollow polystyrene spheres. Close-packed colloidal crystalline arrays were fabricated by simple evaporation of dispersions, whereas nonclose-packed colloidal crystalline arrays were fabricated by exploiting electrostatic interactions between the spheres in aqueous dispersion. Optical properties of the arrays were estimated from angle-resolved reflection spectra. The Bragg diffraction peak of the colloidal crystalline array made of hollow spheres was of shorter wavelength than in the case of solid spheres, not only for the close-packed array but also for the nonclose-packed array. These shifts were caused by a decrease in the effective refractive index n_{eff} with decreasing particle refractive index. We have found that this relationship could be explained by the simple equation $n_{eff} = n_{particle} \phi + n_{solvent} (1 - \phi)$, where ϕ is the volume fraction of the particles, for both close-packed and non close-packed arrays. The current work suggests new possibilities for the creation of advanced colloidal crystals. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2364–2368, 2007

Key words: colloidal crystalline array; hollow spheres; polystyrene spheres; Bragg diffraction; angle-resolved reflection spectra

INTRODUCTION

Colloidal crystalline arrays—three-dimensional periodic lattices of monodisperse colloidal spheres—have recently been examined by many research groups for application as photonic crystals.[1–4]

Photonic crystals have a periodic modulation of their dielectric function and can inhibit certain frequencies of electromagnetic radiation from propagating through specific crystal orientations. Ever since the discovery that a photonic crystal can exhibit a full photonic band gap, namely, a band of frequencies over which an electromagnetic wave cannot propagate in any direction, there have been numerous attempts to fabricate different structures to observe this phenomenon in the visible regime.

Two techniques of manipulating monodisperse colloidal spheres for the generation of crystalline arrays have emerged. One approach involves assembling the spheres into close-packed crystalline arrays through sedimentation or solvent evaporation, and typically relies on nonspecific particle–particle "hard sphere" packing to induce order.[5–11] The second utilizes the long-range repulsive electrostatic interactions of charged colloidal spheres suspended in a liquid medium to construct nonclose-packed crystalline arrays. These arrays self-assemble from monodisperse colloidal spheres containing ionizable surface functional groups. If these spheres are dispersed in a polar medium such as water, the surface groups ionize to form spherical macroions, which are surrounded by a diffuse counterion cloud (the electrostatic double layer).[12–18]

Utilization of composite colloids, in particular core-shell or coated particles, represents an interesting alternative method for the formation of novel photonic crystals.[19–24] Structures fabricated from core-shell colloids, e.g., hollow air-filled spheres, are expected to exhibit unique optical properties. Colloidal crystalline arrays formed from hollow spheres should exhibit different optical properties from those of arrays formed from solid spheres. To the best of our knowledge, there have been many reports about inverted opal, which are three-dimensional porous structure made by use of close-packed crystalline arrays as templates, however, there have been no previous reports on the use of hollow spheres to self-assemble such arrays.

In this article, we have fabricated close-packed and non close-packed colloidal crystalline arrays made of hollow polystyrene spheres and have evaluated their optical properties, using angle-resolved reflection spectra measurements.[25–27] Close-packed arrays were fabricated by simple evaporation of dispersions,

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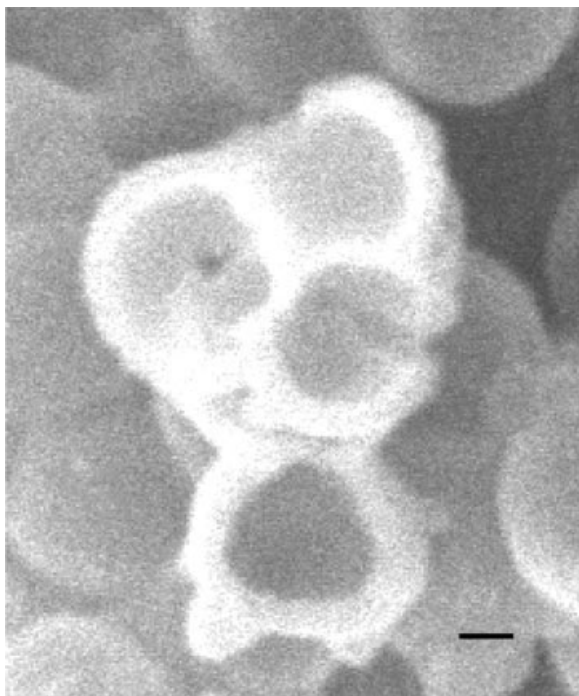
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Figure 1 SEM images of hollow polystyrene spheres. The scale bar in the inset corresponds to 100 nm.

whereas crystalline arrays were fabricated by exploiting electrostatic interactions between the spheres in aqueous dispersion.

EXPERIMENTAL

Hollow polystyrene spheres and solidones (both of diameter 400 nm, the standard deviation is about 10% of the diameter) were purchased from JSR, Japan. From SEM images, e.g., as shown in Figure 1, the ratio of the inner diameter to the outer (or total) diameter of the hollow spheres was $\sim 2/3$, and the volume fraction of hollow part of the sphere was 0.30. The spheres were shaken with an excess of mixed bed ion-exchange resin (AG501-X8(D), Bio-Rad Laboratories, Hercules, CA) in the aqueous suspension (pH = 6) to reduce ionic impurities.

The close-packed array was prepared by injecting a colloidal dispersion of the spheres into a fluidic cell composed of two flat glass substrates with two spacers ($t = 0.05$ mm) sandwiched between them.[25–27] The cell had two openings of the same thickness as the spacer, with a fluid reservoir connected to one of the openings. After the dispersion was injected into the reservoir, it entered the cell by capillary action. The close-packed array grew gradually from the vicinity of the other opening, and the sample was dried by solvent evaporation at room temperature.

The nonclose-packed array was prepared by shaking the spheres with an excess of mixed bed ion-

exchange resin to reduce ionic impurities in aqueous dispersion, and subsequent injection into a quartz cell.

Optical properties of the colloidal crystalline array were evaluated by measuring their reflection spectra at normal incidence, using a multi-channel spectrometer (Soma Optics, Fastevert S-2650). Structural analysis of the samples was performed by angle-resolved reflection spectroscopy. These spectra were measured by changing the angle of incidence θ between the beam and the normal of the sample surface from 9° to 46°and by collecting the light scattered in the Bragg configuration. The Bragg equation is given by eq. (1):

$$m\lambda_{\text{peak}} = 2\,d_{111}(n_{\text{eff}}^2 - \sin^2\theta)^{1/2} \qquad (1)$$

where m is the order of diffraction; λ_{peak} is the wavelength of the Bragg diffraction peak; d_{111} is the interplanar spacing between (111) planes; θ is the angle between the incident light and the normal to the diffraction planes (at normal incidence, $\theta = 0°$); and n_{eff} is the mean effective index of this crystalline lattice. The wavelength λ_{peak} of each reflection peak was
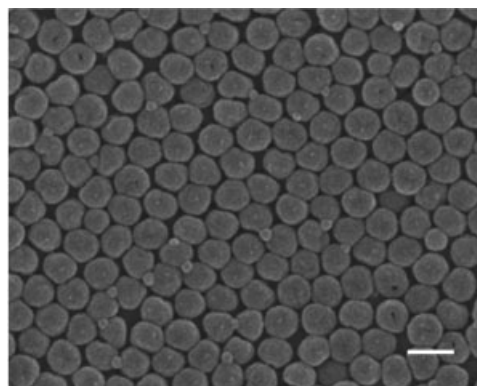
(a)
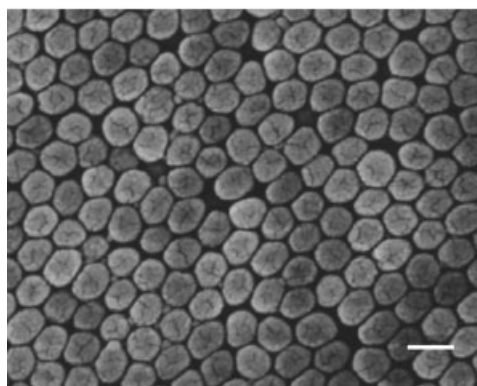
(b)

Figure 2 SEM images of close-packed colloidal crystalline arrays of (a) hollow polystyrene spheres and (b) solid polystyrene spheres. The scale bar in the inset corresponds to 500 nm.
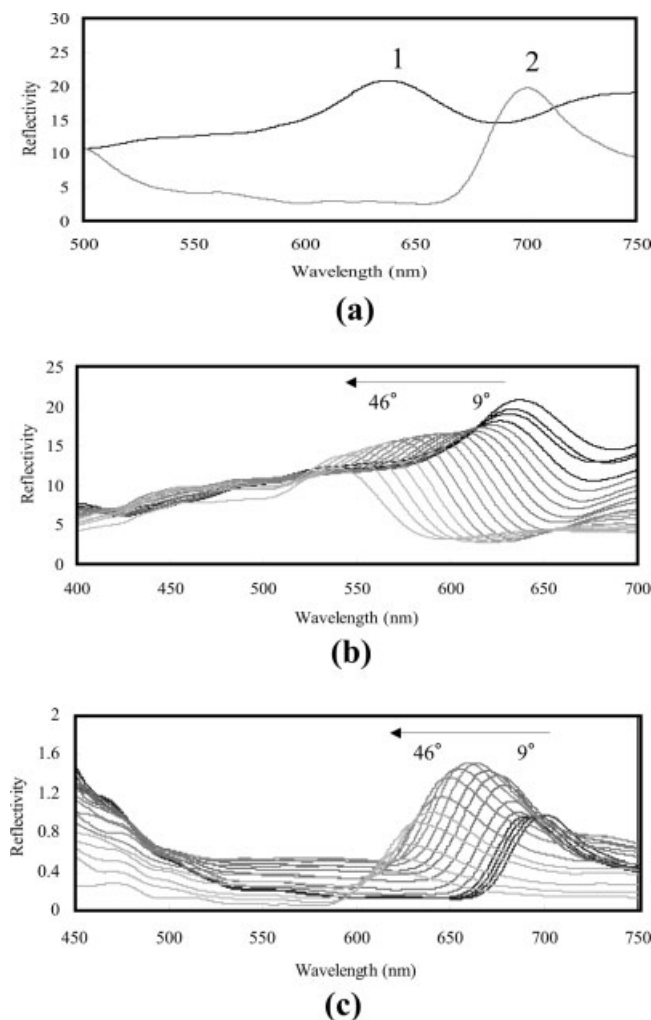
Figure 3 (a): Reflection spectra of close-packed colloidal crystalline arrays made of (1) hollow polystyrene spheres and (2) solid polystyrene spheres. (b, c): Angle-resolved reflection spectra of close-packed colloidal crystalline arrays made of hollow and solid polystyrene spheres.

plotted against θ. The interplanar spacing d_{111} and n_{eff} were determined by fitting the Bragg equation to the plotted data.

RESULTS AND DISCUSSION

Close-packed colloidal crystalline array of hollow spheres

Figure 2 shows scanning electron microscopy (SEM) images of the crystalline arrays made from hollow and solid polystyrene spheres. Both types of spheres formed hexagonal close-packed multiple layer structures. However, the crystallinity of these structures was not high enough for the materials to exhibit sharp diffraction peaks, because the polydispersity of these particles was above 10%.

Figure 3(a) shows the reflection spectra of the arrays made from hollow and solid polystyrene spheres. The

(111) planes of the colloidal crystalline array were oriented parallel to the surface of the supporting substrate. In these measurements, the incident light and detector were both oriented perpendicular to the (111) plane of this lattice. The broad Bragg diffraction peak of the hollow-sphere array was at a shorter wavelength than that of the solid-sphere array. This shift may have been caused by either decreasing lattice constant or decreasing refractive index. To identify precisely the factor responsible for this shift, angle-resolved reflection spectra measurements were performed. Figures 3(b,c) show the angle dependence of reflection spectra of the hollow-sphere array and solid-sphere array, respectively. The spectrum evolved gradually with increasing θ. The peak wavelength of the reflection corresponds to the resonance on a set of (111) planes as a function of the angle. When the incident light was rotated toward the (111) surface of the crystal within the zx- and zy-planes, the position of the diffraction peak shifted to a shorter wavelength. As both spectra showed blue shifts, it could be deduced that these colloidal crystalline arrays were face-centered cubic. The wavelength λ_{peak} of each reflection peak is plotted against θ, and the interplanar spacing d_{111} and n_{eff} were determined by fitting the Bragg diffraction eq. (1) to the plotted data. Figure 4 shows the relationship between incident angle and peak of reflection spectra for these close-packed colloidal crystals. The very close fit also supports the fact that these structures undergo Bragg diffraction. The fit to eq. (1), d_{111} and n_{eff} of the arrays were all derived from angle-resolved diffraction spectra. The refractive index of the hollow-sphere array was smaller than that of the solid-sphere array. This must have been caused by the differences in the spheres' interiors (polystyrene- or air-filled). The effective refractive index can be approximated by eq. (2):

$$n_{eff} = n_{particle}\phi + n_{air}(1 - \phi) \tag{2}$$

where φ is the filling fraction of the volume occupied by the particles (φ = 0.74 for the close-packed fcc
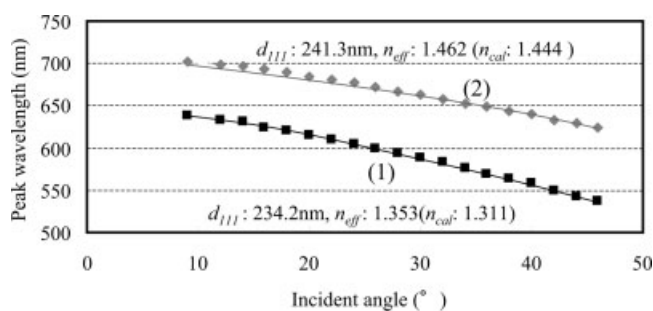

Figure 4 Wavelength of the reflection peak versus incident angle of light for close-packed colloidal crystalline arrays made of (1) hollow polystyrene spheres and (2) solid polystyrene spheres. The solid lines are the curves fitted using the Bragg law, eq. (1).

Figure 5 Wavelength of the reflection peak versus incident angle of light for nonclose-packed colloidal crystalline arrays made of (1) hollow polystyrene spheres and (2) solid polystyrene spheres. The solid lines are the curves fitted using the Bragg law, eq. (1).
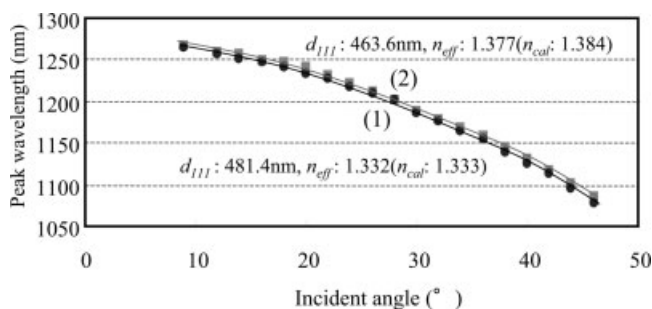

Figure 7 Schematic illustrations of close-packed and non-close-packed colloidal crystalline arrays made of hollow polystyrene spheres.

structure). n_{particle} and n_{air} represent the refractive indices of polystyrene (1.60) and air (1.00), respectively. In a hollow sphere, $n_{\text{particle}} = n_{\text{polymer}}\phi' + n_{\text{air}}(1 - \phi')$, where ϕ' is the volume fraction of the polymer part and $1 - \phi'$ is the volume fraction of the inner air space. In this case, as ϕ' is ~ 0.70, n_{particle} must be 1.42. In Figure 4, n_{cal}, which is the effective refractive index derived from this equation, is also shown. There is close agreement with the experimental results. We think that the reason for a slightly larger n_{eff} compared to n_{cal} is due to remaining water in either the outer or inner section of the sphere after evaporation.

These results indicate that n_{eff} of close-packed colloidal crystalline arrays of hollow spheres could be calculated from eq. (2).

Nonclose-packed colloidal crystalline array of hollow spheres

Figure 5 shows the relationship between incident angle and peak of reflection spectra of the non close-packed colloidal crystalline arrays made of hollow polystyrene spheres and made of solid polystyrene spheres. d_{111} and n_{eff} of the crystalline arrays were derived from fits of angle-resolved diffraction spectra
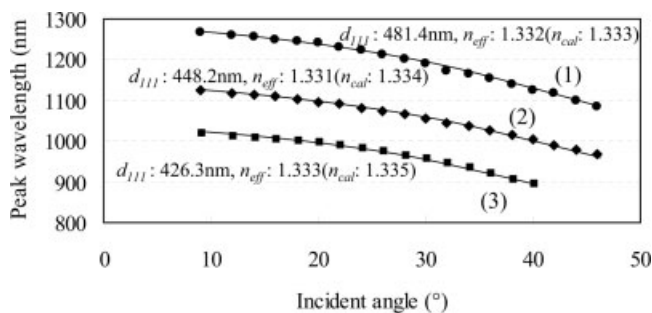

Figure 6 Wavelength of the reflection peak versus incident angle of light for nonclose-packed colloidal crystalline arrays made of hollow polystyrene spheres of (1) 20 vol %, (2) 25 vol %, and (3) 30 vol %. The solid lines are the curves fitted using the Bragg law, eq. (1).
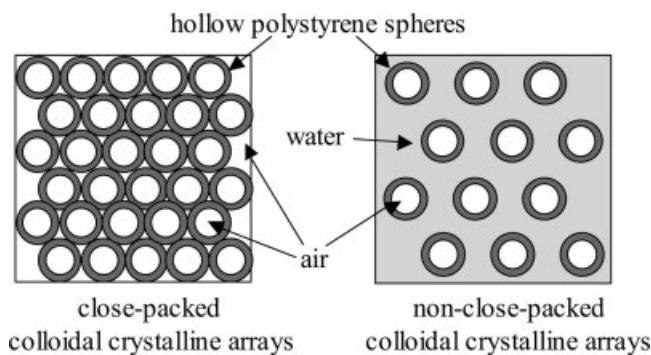
to eq. (1) as before (Fig. 4). In each case, for these particles, d_{111} of the non close-packed crystalline arrays was larger than that in the close-packed case, i.e., non close-packed arrays were formed by electrostatic repulsion forces. The refractive index of hollow-sphere array was smaller than that of solid-sphere array, as well. This result must have originated from the presence of polystyrene versus air in the interior of the spheres. The effective refractive index could again be approximated by eq. (2), and n_{particle} and n_{air} represented the refractive indices of particle and air, respectively. In Figure 5, n_{eff} derived from the equation are again shown, and agreement with the experimental results was excellent, as before.

Figure 6 shows the effect of sphere concentration on the relationship between incident angle and peak of reflection spectra of the non close-packed colloidal crystals made of hollow spheres. Fits to eq. (1), d_{111} and n_{eff} were derived. d_{111} decreased and n_{eff} increased with increasing of volume fraction of the hollow spheres. This behavior resulted from increasing the hindered effect of sphere volume and increasing refractive index of the crystal array. In Figure 6, n_{eff} derived from the equation are again shown, and agreement with the experimental results was excellent, as before.

These results support that n_{eff} of the colloidal crystalline arrays of hollow spheres were simply explained by the model defined by eq. (2) and Figure 7, for both close-packed and non close-packed arrays.

CONCLUSIONS

We have evaluated the optical properties of close-packed and non close-packed colloidal crystalline arrays made of hollow polystyrene spheres. Close-packed colloidal crystalline arrays were fabricated by evaporation of a dispersion, whereas non close-packed colloidal crystalline arrays were fabricated by taking advantage of electrostatic interactions between spheres in aqueous dispersion. Optical properties

were evaluated using angle-resolved reflection spectra measurements. The Bragg diffraction peak of colloidal crystalline arrays made of hollow spheres was at a shorter wavelength than that of solid spheres, not only for close-packed arrays but also for non close-packed arrays. These shifts were caused by a decrease in the effective refractive index n_{eff} with decreasing particle refractive index. We have found that this relationship was explained by the simple equation $n_{eff} = n_{particle}\phi + n_{solvent}(1 - \phi)$, which applied to both array types.

References

1. Adv Mater 2001, 13(6); A special issue on Photonic Crystals.
2. MRS Bull 2001, 26, 608; A special issue on Materials Science Aspects of Photonic Crystals.
3. Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. Adv Mater 2000, 12, 693.
4. van Blaaderen, A.; Ruel, R.; Wiltzius, P. Nature 1997, 385, 321.
5. Davis, K. E.; Russel, W. B.; Glantschnig, W. J. Science 1989, 245, 507.
6. Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. Nature 1993, 361, 26.
7. Miguez, H.; Meseguer, F.; Lopez, C.; Mifsud, A.; Moya, J. S.; Vazquez, L. Langmuir 1997, 13, 6009.
8. Park, S. H.; Xia, Y. Langmuir 1999, 15, 266.
9. Im, S. H.; Lim, Y. T.; Suh, D. J.; Park, O. O. Adv Mater 2002, 14, 1367.
10. Wong, S.; Kitaev, V.; Ozin, G. A. J. Am Chem Soc 2003, 125, 15589.
11. Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. Chem Mater 1999, 11, 2132.
12. Krieger, I. M.; O'Neill, F. M. J Am Chem Soc 1968, 90, 3114.
13. Hiltner, P. A.; Krieger, I. M. J Phys Chem 1969, 73, 2386.
14. Clark, N. A.; Hund, A. J.; Ackerson, B. J. Nature 1979, 281, 57.
15. Goodwin, J. W.; Ottewill, R. H.; Parentich, A. J Phys Chem 1980, 84, 1580.
16. Carlson, R. J.; Asher, S. A. Appl Spectrosc 1984, 38, 297.
17. Pusey, P. N.; van Megen, W. Nature 1986, 320, 340.
18. Rundquist, P. A.; Photinos, P.; Jagannathan, S.; Asher, S. A. J Chem Phys 1986, 91, 4932.
19. Rogach, A. L.; Sucha, A.; Carso, F.; Sukhorukov, G.; Kornowshi, A.; Kershaw, S.; Mohwald, H.; Eychmuller, A.; Weller, H. Adv Mater 2000, 12, 333.
20. Kalinina, O.; Kumacheva, E. Chem Mater 2001, 13, 35.
21. Breen, M. L.; Dinsmore, A. D.; Pink, R. H.; Qadri, S. B.; Ratna, B. R. Langmuir 2001, 17, 903.
22. Velikov, K. P.; Moroz, A.; van Blaaderen, A. Appl Phys Lett 2002, 80, 49.
23. Graf, C.; van Blaaderen, A. Langmuir 2002, 18, 524.
24. Liang, Z.; Susha, A.; Carso, F. Chem Mater 2003, 15, 3176.
25. Ishii, M.; Nakamura, H.; Nanano, H.; Tsukigase, A.; Harada, M. Langmuir 2005, 21, 5347.
26. Nakamura, H.; Ishii, M.; Tsukigase, A.; Harada; Nanano, H. Langmuir 2005, 21, 8918.
27. Nakamura, H.; Ishii, M.; Tsukigase, A.; Harada, M.; Nanano, H. Langmuir 2006, 22, 1268.