Crystal thickness and sphere dispersion dependence of the photonic band gap of silica colloidal crystals

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Experimental results demonstrate that the band gap of colloidal suspension crystal changes with both the thickness of crystal and the dispersity of micro-spheres. As the thickness decreases, a red shift of band gap is observed, and there is a maximum of red shift. The values of the maximum red shifts are dependent on the standard deviations of micro-spheres. The experimental results are consistent with theoretical calculation. As the colloidal suspension crystal is assembled from micro-spheres with a standard deviation of 8.4% in a thick cell, an incident angles independent broadband is observed, which is explained as an amorphous structure. Two amorphous models are discussed.

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Photonic band gap (PBG) crystal, which holds the key to continuous progress towards all-optical integrated circuits, has been an active research area since the initial predictions by Yablonovitch[1] and John[2]. In order to construct structures, in which band gaps are centered in the visible region, the length scale of the periodicity of photonic crystal (PC) must be of the order of hundred of nanometers. It is still quite challenging and expensive to fabricate three-dimensional (3D) PC materials with band gaps in visible wavelength by some methods such as lithographic fabrication. Therefore, for the study on its physical properties in the visible wavelength, colloidal crystals, in which dielectric micro-spheres spontaneously self-assemble into ordered arrays of face-centered-cubic (fcc), are studied relatively early and extensively[3−10]. This self-assembling approach does not require expensive instruments, and is easy to fabricate samples with optional thickness. Thickness dependent property is an important characteristic of PC. The interesting phenomenon of thickness dependent property of band gap in opals was reported[11]. However, systematic investigation of the thickness and dispersity dependent properties of band gap in colloidal suspension crystals is very important and still lack.

In this work, the colloidal suspension crystals with thickness from 30 μm to 1 mm and self-assembled by the particles with a series of standard deviations are studied. The experimental results demonstrate that the band gap of colloidal suspension crystal depends on both the thickness and the dispersity of micro-spheres, and imply the colloidal amorphous structure.

In this work, high quality cells were fabricated. The thicknesses of the lower part (34 mm) of the cells are 1, 0.2, 0.1, 0.07, and 0.03 mm, respectively. The cell top of 25 mm is in the shape of upside down triangle, as shown in Fig. 1.

During the process of crystal growth, there is a distinct interface boundary between the transparent crystallization part and the ivory-white random part. This boundary moves from the bottom to the top of the cell. As the transparent crystallization part filled up the lower part of 34 mm, the redundant spheres in the upside down triangle cell was drawn out to make sure the same height of 34 mm in every cell. It takes almost three months to grow a stable sample in the cell of thickness of 1 mm, and less than one month for 0.07- and 0.03-mm cells. The process of the colloidal crystal growth in the thin cell is much quicker than that in the thick ones.

The fabrication results and processes of colloidal crystals are dependent on the concentration, the dispersity and the size of the micro-spheres, the volume of the cell, the solvent, and its pH value. Generally, high concentration (>3.5%) results in fcc structure[12]. In this work, the concentrations of all samples are the same of 25%, therefore only the fcc structure appears. In the thin cell, the indeed single crystal is got, because whether by eye or by microscope, no scattering point is found in the thin cell. However, in the thick cell, a lot of scattering points are observed.

After the silica colloidal crystals had formed, their transmission spectra were measured by a spectrophotometer (Shimadzu UV-3101PC). Because the band gaps of silica colloidal crystals depend on the height of the detecting point, the transmission spectra were measured at the same height (16 mm to the bottom, and 18 mm to the top of the crystal).

Figure 2 shows the transmission spectra of two colloidal crystals. These two crystals are assembled from

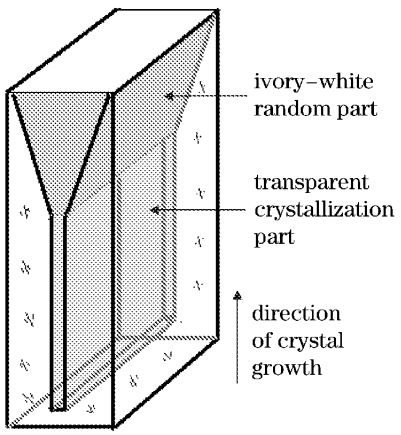

Fig. 1. Sketch shows the fabrication of the samples.

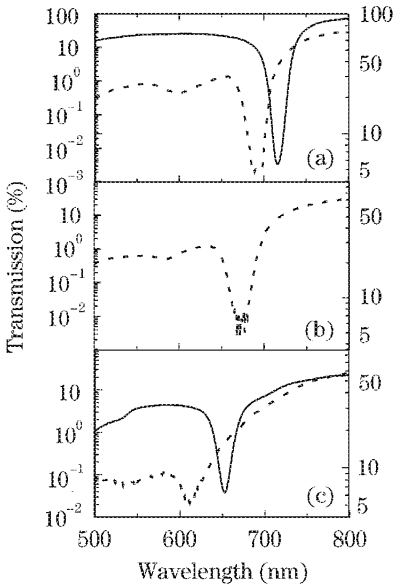

Fig. 2. The transmission spectra of colloidal crystal. Dashed lines: in the cell with thickness of 1 mm; solid lines: in the cell with thickness of 0.07 mm. Standard deviation of the micro-spheres is 3.6%, and the angles of incident light are 0° (a), 20° (b), and 45° (c).

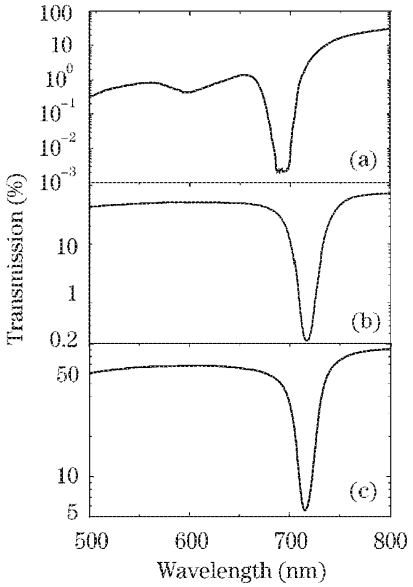

Fig. 3. The transmission spectra of colloidal crystal, in which the thicknesses of the cells are 1 (a), 0.2 (b), and 0.07 mm (c), respectively. The standard deviation of the micro-spheres is 3.6%, and the angle of incident light is 0°.

micro-spheres with the same standard deviation of 3.6% but with different cell thicknesses of 0.07 and 1 mm, respectively. The spectra, in which the peaks have blue shift with the increase of incident angles, demonstrate that the colloidal crystals in both thin and thick cells have non-complete PBGs. The (111) face of fcc crystal is along the wall surface, because the longest wavelength appears at perpendicular incidence. The spectra in Fig. 2 show that the peak wavelengths of PBG of dashed lines are shorter than these of solid lines, although they are assembled from micro-spheres with same diameter. As the incident angle is 0°, the peak of the band gap in 0.07-mm cell has a red shift of 24 nm as compared with that in 1-mm cell.

The transmission spectra of colloidal crystals in a series of thicknesses, such as 1, 0.2, 0.1, 0.07, and 0.03 mm, were measured. As the colloidal crystal is assembled from micro-spheres with standard deviation of 3.6%, and the incident angle is 0°, the peak wavelengths of PBG in 0.2-, 0.1-, 0.07-, and 0.03-mm cells are the same. The transmission spectra of these in 1-, 0.2-, and 0.07-mm cells are shown in Fig. 3, which demonstrate that the maximum red shift in thin cells is of 24 nm compared with that in 1-mm cell.

Furthermore, the transmission spectra of colloidal crystal assembled from micro-spheres with a series of dispersity in a series of thicknesses were measured in this experiment. Experimental results demonstrate that the band gap of colloidal crystal changes with both thickness and the dispersity of the micro-spheres. The experimental results of the maximum of red shift, $\Delta\lambda/\lambda$, and the calculation results of maximum of increment of lattice vector are shown in Table 1.

This phenomenon is similar to the height dependent band gaps of silica colloidal crystals. For excluding the effect on the height, the transmission spectra were measured at the same height (16 mm to the bottom, and 18 mm to the top of the crystal) of the detecting point. For comparison, height dependent transmission spectra of a colloidal crystal, with cell thickness of 0.2 mm and standard deviation of 4.5%, was measured. The red shift of the stop band is 13.6 nm for the height of the center of the detecting point changing from 5 to 23 mm, which is less than the effect of thickness (35 nm).

Table 1. Dispersity Dependence of the Maximum of Red Shift

Standard Deviation (%)	Maximum of Red Shift, $\Delta\lambda$ (nm)	$\Delta\lambda/\lambda$ (%)	Maximum of Increment of Lattice Vector, Δa (nm)
3.2	17	3.1	9.7
3.6	24	3.4	12.0
4.5	35	5.8	17.7
8.4	106	13.7	56.6

We have written a program which searches for the approximate scale of primitive lattice vector (defined as a) by Powell's quadratic convergent method[13], based on the wavelength of the band gap. With the decrease of the cell thickness, a is increasing. For example, considering the sample with standard deviation of 3.6%, a is 300.21 nm for the 1-mm cell and 312.22 nm for the 0.02−0.07 mm cell. Furthermore, the maximum increase of a is corresponding to the standard deviation, as shown in Table 1.

Dispersity dependence of the minimum of the transmission and bandwidth are listed in Table 2. As the cell thick is 0.07 mm, the bandwidths are narrow and almost not changing with the standard deviation except that of 8.4%, and the narrow bandwidths imply long-range order of the particles in these thin cells. On the contrary, in thick cell (1 mm), the bandwidths are broadening with the standard deviations. The minima of the transmission

Table 2. Dispersity Dependence of the Minimum of the Transmission and Bandwidth

Standard Deviation (%)	Minimum of the Transmission (%)				Bandwidth (nm)	
	0.07-mm Cell		1-mm Cell		0.07-mm Cell	1-mm Cell
	0°	20°	0°	20°		
3.2	0.85	1.18	0.0015	0.0047	18.1	19.8
3.6	5.2	5.7	0.002	0.024	18.5	24.7
4.5	6.9	6.4	0.032	0.031	19.8	34.4
8.4	12.8	5.58	0.08	0.08	25.9	90

listed in Table 2 also demonstrate some important message. In the thick cell and standard deviation of less than 4%, the minimum of the transmission of perpendicular incidence is less than that of 20° incidence, which approaches the result of standard fcc structure. However, the minimum of the transmission does not change with the incidence angle for the standard deviation of 8.4%. In the thin cell with large standard deviation spheres, another novel phenomenon appears. The minimum of the transmission at perpendicular incidence is larger than that of 20° incidence. It means the anamorphic fcc structure appears. The weak light absorption results in lower particle density on (111).

The self-assembling results from the balance of many forces, such as gravity, static repulse force between the micro-spheres, and interactive force between the vertical cell walls and the micro-spheres. This balance determines the interspaces (the spaces between the surfaces of micro-spheres). Generally, self-assembling has a potential to form rigorous fcc single crystal if the micro-spheres are uniform. However, the dispersity of micro-spheres always exists, which makes the colloidal crystal depart from rigorous fcc single crystal if the spheres are densely deposited. The gravity makes the interspaces diminish tending to dense deposition, while the others make the interspaces enlarge.

In the thin cell, interactive force between the cell wall and the micro-sphere is strong enough to overcome the gravity to make the interspaces broad enough to form the rigorous fcc single crystal, because the interactive force is dependent on high order exponent of the distance between wall and sphere. The rigorous fcc single crystal structure is the stablest self-assembling structure, therefore, as it is got, the interspaces will not enlarge again with the cell thinning. It results in the existence of the maximum of red shift.

In the thin cell with large standard deviation spheres, much broader interspaces are needed to compensate for forming the rigorous fcc single crystal. Then, the anisotropic property of the interactive force between the cell wall and the micro-sphere makes the anamorphic fcc structure appear. The experimental results relating to deviation are consistent with theoretical calculation in the last column in Table 1. The theoretical calculation for thickness are also consistent with the experimental results.

In the thick cell, the interactive force between the cell wall and the micro-sphere could be neglected because the interactive force is dependent on high order exponent of the distance between wall and sphere. Therefore the interspaces are not broad enough to compensate the deviation of the spheres for forming a rigorous fcc single crystal, whose structure is similar to Fig. 5(b).

Figure 4 shows the transmission spectra of the colloidal crystals, which are assembled from micro-spheres with a standard deviation of 8.4%, in the cells with thicknesses of 0.07, 0.2 and 1 mm, respectively. As shown in Fig. 4, the peaks of band gaps in thin cell (solid and dashed lines) are relative narrow and change with the incident angle. This demonstrates that a non-complete PBG appears in these two thin cells. By contrast, in 1-mm cell (dashed dot lines), a broad and shallow peak almost does not change with the incident angle.

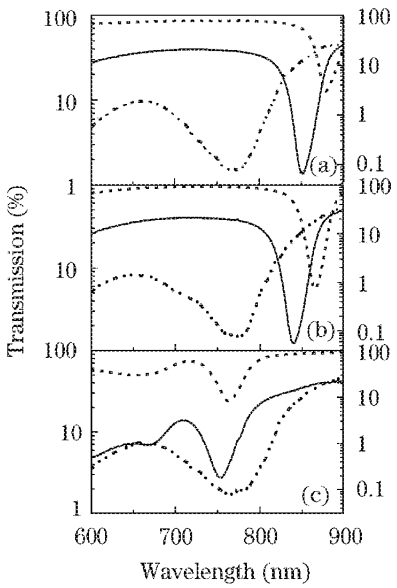

Fig. 4. The transmission spectra of colloidal crystal, in which the thicknesses of the cells are 0.07, 0.2 and 1 mm corresponding to dashed lines, solid lines (left scale) and dashed dot lines (right scale), respectively. The standard deviation of the micro-spheres is 8.4%, and the angles of incident light are 0° (a), 20° (b), and 45° (c).

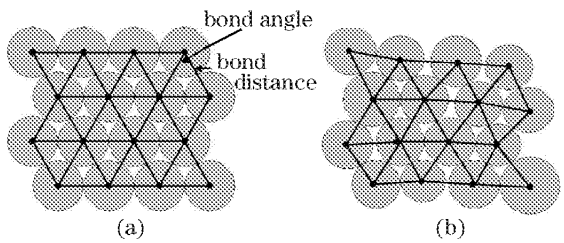

Fig. 5. The sketches of rigorous crystal (a) and continuous network of amorphous crystal (b).

About the stability, all of the samples can be kept two years without change, except the dashed dot line in Fig. 4, which was measured just after the crystal growth, then its band gap changed shallowly month by month. This special broad shallow band gap can be explained as an amorphous PC. The phenomenon of incident angles independent broad PBG can be explained as the decrease of the symmetry of the lattice and the large irregularity in the amorphous colloidal crystal.

A well-known model for amorphous crystal is the short-range order structure. Every short-range order micro-crystal has different orientation. It results that every direction has micro-crystals of all orientations, from L point to W point. One orientation has a sharp band gap, and the combining of all orientations forms a broadband.

Here, based on the dispersivity and thickness effects discussed above, we propose another model, continuous network model, in which the lattice is the same as that of the rigorous single crystal, but the bonds lack unity[14]. This is impossible in amorphous semiconductors because of the identical atoms. However, for PC, it is a general structure because dispersivity of the man-made micro-spheres always exists. For micro-spheres with large standard deviation in thick cell, in which the interspace between micro-spheres is small, the bond angles and bond distances cannot keep identical.

Figure 5(a) shows a rigorous fcc single crystal model, in which the bond angles and bond distances are identical, and the bonds connect to form beelines. Figure 5(b) shows a continuous network model, in which the bonds connect to form flexural lines. It can be partly used to explain the results of dashed dot line in Fig. 4, although its structure cannot be validated by electron microscopy for its liquid property.

Theoretical studies demonstrate that non-complete PBG in fcc single silica colloidal crystal results from its high symmetry. By decreasing the symmetry of the lattice through the introduction of a two-point basis set, which produces the diamond lattice, degeneracy in the bands is lifted and a complete PBG is obtained[15]. Many structures with decreasing symmetry have been proposed, such as two-dimensional (2D) square format and hexagonal lattices, 2D single- and double-rod square structures[16–18], especially, complete PBG was shown in quasi-crystals[19]. In this work, it can also be explained as the decrease of the symmetry of the lattice by irregularity in amorphous colloidal crystal.

The colloidal crystals with a series of thicknesses are self-assembled from micro-spheres with a series of standard deviations. The spectral experimental results demonstrate that the peak wavelength of band gap in colloidal crystal depends not only on the thickness, but also on the dispersity of micro-spheres. In comparison with thick cell, there is a maximum of red shift of band gap in thin cell, which depends on the standard deviation of micro-spheres, such as the maxima of red shift of 17, 24, 35, and more than 106 nm corresponding to the standard deviation of 3.2%, 3.6%, 4.5%, and 8.4%, respectively. These results imply that in the thin cell the interspaces between micro-spheres are broadening, which brings about the appearance of rigorous face-center single crystal, while in the thick cell the narrow interspaces cannot compensate for the deviation of the micro-spheres which may makes the bonds of face-center crystal not the same. As the colloidal crystal is assembled from micro-spheres with standard deviation of 8.4% in a cell with the thickness of 1 mm, an incident angles independent shallow broad PBG has been observed. This phenomenon can be explained as amorphous crystal forming, here a continuous network structure model with disunity bonds is proposed, together with the short-range order structure, for explaining the phenomena. The incident angles independent broad PBG results from the decrease of the symmetry of the lattice by large irregularity in the amorphous colloidal crystal.

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