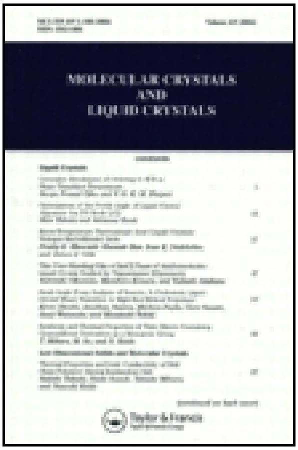

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Diffraction Color Developed by Self-Assembly of Silica Particle Arrays

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Version of record first published: 22 Sep 2010

To cite this article: Tae Hyeon Kim, Hyung Jun Kim, Taek Seung Lee & Won Seok Lyoo (2007): Diffraction Color Developed by Self-Assembly of Silica Particle Arrays, Molecular Crystals and Liquid Crystals, 464:1, 153/[735]-159/[741]

To link to this article: http://dx.doi.org/10.1080/15421400601030787

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 153/[735]–159/[741], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601030787

Diffraction Color Developed by Self-Assembly of Silica Particle Arrays

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Thin films of ordered arrays were fabricated with size-controlled silica spheres by solvent evaporation method. The ordered arrays could transmit a light of specific wavelength, which was significantly dependent on the particle size and confirmed using UV transmission spectroscopy. The stop band in UV spectrum was blue-shifted with a decrease in particle size, which can be explained by Bragg's diffraction law. By theoretical calculation, the colloidal crystal prepared with silica particles of 480 nm should show maximum transmission at 1056 nm and the self-assembled multilayer prepared with 560 nm-sized particles should exhibit stop band at 1390 nm, which, however, showed deviations of stop band between theoretical and experimental values. The deviation between theoretical and experimental values can be regarded as a result from the defects and disordered area in the colloidal crystal.

Keywords: colloidal crystal; ordered array; silica spheres

Financial support from Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE) is gratefully acknowledged (Grant No. RTI04-01-04).

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INTRODUCTION

Photonic colloidal crystals have recently been attracted much attention for their potential applications such as the unique ways of controlling the propagation of light and many researches are being carried out in terms of their fabrication and particular optical effects [1,2]. Amongst the useful materials for building crystal structures, silica is found to be most effective due to easy preparation method and dimensional stability [3]. Silica particles are synthesized from tetraethyl orthosilicate (TEOS) by the simple well-known sol-gel method. The size of silica spherical particles can be controlled by adjusting the concentration of TEOS and catalyst, ratio of TEOS and catalyst, and reaction time.

A number of methods have been developed for fabrication of colloidal crystals such as the solvent evaporation method [4–6]. Colloidal crystals have been fabricated into a 3-dimensional face-centered cubic structure (FCC). Because of the regulative arrangement of particles, they show photonic band gap property related to their particle size. The λ_{max} of photonic band gap can be calculated by Bragg's law and be confirmed with the stop band in its transmission spectrum. However, when colloidal crystals have been fabricated into a 2-dimentional hexagonal structure, they show different optical properties compared to the colloidal crystals with a 3-dimentional structure.

In this paper, silica spherical particles were synthesized by sol-gel reaction, colloidal crystals were fabricated into mono- and multi-layered structures and their optical properties were characterized with UV transmission spectroscopy in connection with their array morphology.

EXPERIMENTAL

Reagents and Measurements

TEOS were purchased from Samchen Chemical and ammonium hydroxide was used as a catalyst for the sol-gel reaction. UV-visible spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. The photographs of scanning electron microscopy were taken using Topcon SM-500. The size of silica particle was measured with Scope Eye Image Analysis software.

Fabrication of Colloidal Crystals

Silica spherical particles (0.04 g) were dispersed into distilled water (40 ml) using a sonicator in a 50 ml beaker. And then the temperature of this solution was increased to 60°C and a glass slide substrate was immersed into the solution perpendicularly. After evaporating water, the glass slide substrate was put into vacuum oven and dried at 100°C for 24 h. After drying, translucent and color-changeable colloidal crystals were obtained.

RESULTS AND DISCUSSION

Submicron-sized silica particles were prepared by the conventional low-temperature sol-gel reaction [7–9]. Average diameters of these sphere-shaped particles were measured about 560 nm and 480 nm, and the standard deviations were 20 nm and 10 nm, respectively according to the reaction condition.

Colloidal crystals were fabricated by the solvent evaporation method and the process is illustrated schematically in Figure 1. As water was evaporated from the surface of the suspension solution, silica particles moved ahead meniscus at the glass-water interface. After silica particles were anchored on the surface of glass substrate, water between neighboring two particles anchored on glass substrate was evaporated and small meniscus was created. Then silica particles were made close packed structure by the capillary force induced by small meniscus, and stabilized by hydrogen bonding between hydroxyl groups on the surface of silica particles.

In the case of low silica particle concentration (0.04 g/40 ml H_2O), silica particles were self-assembled into hexagonal structure (Fig. 2(a) and (c)). In the starting area of self-assembling, the array showed tetragonal structure (top area of the photo in Figure 2(b)). After stabilizing self-assembling, most of the array appeared hexagonal structure that had some line defects induced by irregularly sized

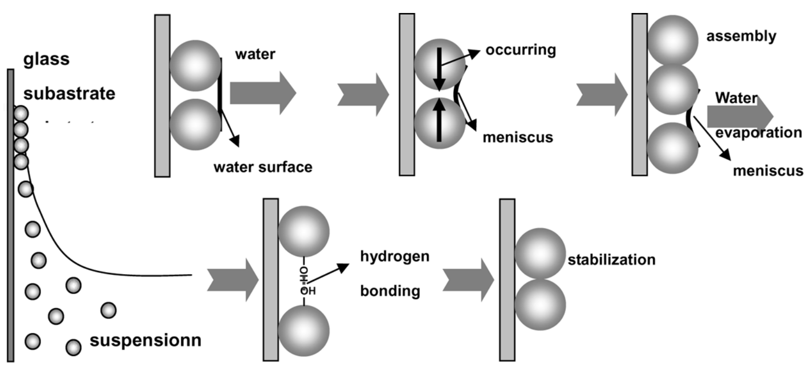


FIGURE 1 Schematic diagram for the solvent evaporation method.

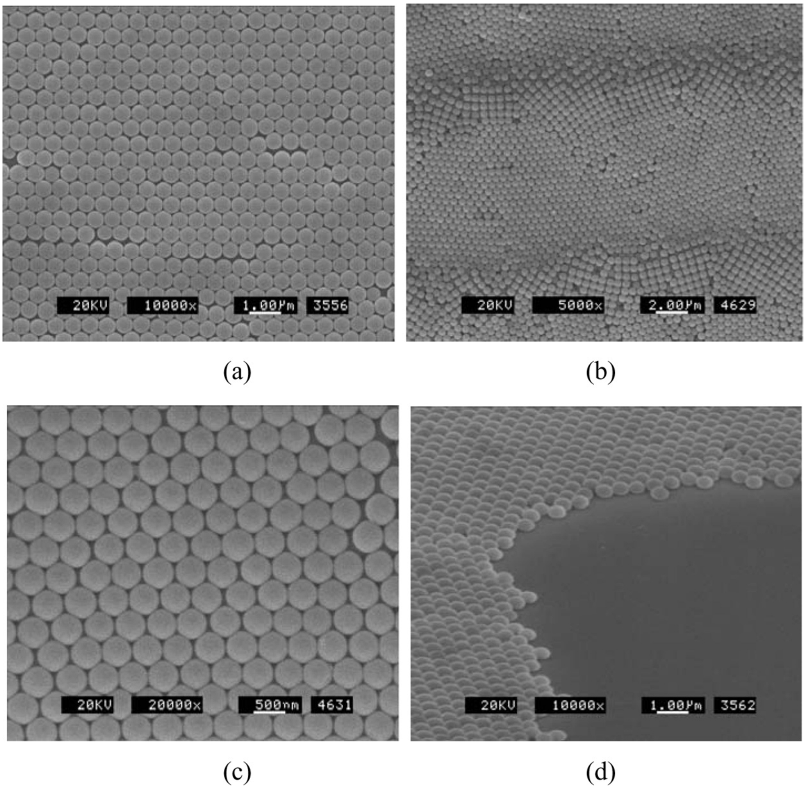


FIGURE 2 SEM photographs of 2-dimentional structure fabricated with silica particles of 560 nm (a), (d) and 480 nm (b), (c).

particles. The 2-dimentional monolayer was confirmed by tilted SEM photograph (Fig. 2(d)).

On the other hand, in the case of high silica particle concentration (0.4 g/40 ml H_2O), silica particles were fabricated into multi-layered colloidal crystal structure that was assembled into (FCC) as well known in previous report [10]. We could confirm the FCC structure in the surface of ordered array that showed hexagonal structure (Fig. 3).

The optical properties of colloidal crystals were measured with UV transmission spectroscopy as shown in Figure 4. Photonic band gap of multi-layered colloidal crystal is estimated by the equation as follows [11];

$$\lambda_{\max} = 2\, d_{111}(\mathrm{n}_{average}{}^{2} - \sin^2\phi)^{1/2} \tag{1}$$

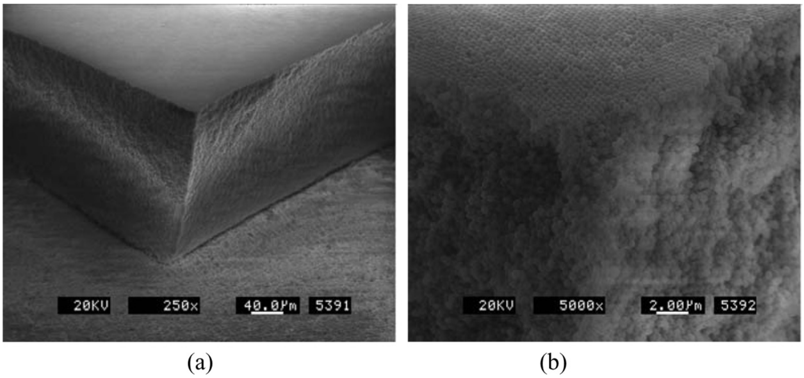


FIGURE 3 SEM photographs of 3-dimentional structure fabricated with 480 nm-sized silica particles.

$$n_{average}{}^2 = f_{Silica} n_{Silica}{}^2 + f_{Air} n_{Air}{}^2 \qquad (2)$$

$$d_{111} = (2/3)^{1/2} D \qquad (3)$$

where D is particle size, d_{111} is spacing between (111) planes, $n_{average}$ is average refractive index, ϕ is incident angle, f_{Silica} and f_{Air} are volume fraction of silica particle and air and n_{Silica} and n_{Air} are refractive indices of silica particle and air, respectively. D was calculated using Scope Eye Image Analysis program to 480 nm and 560 nm. The values of n_{Silica} and n_{Air} are known to be 1.45 and 1.00, and the values of f_{Silica} and f_{Air} in the case of FCC structure are known to be 0.74 and 0.26,

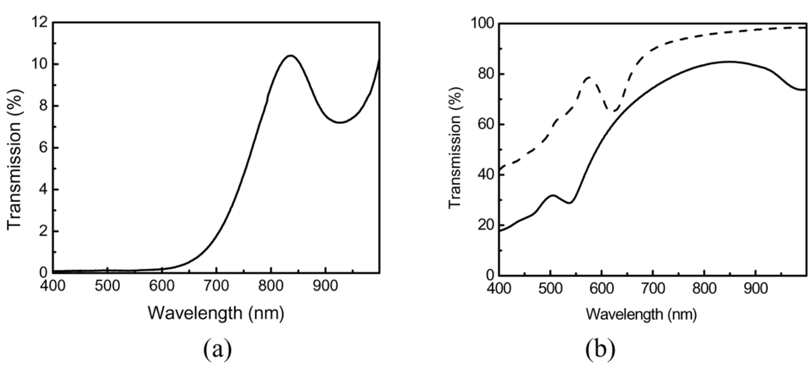
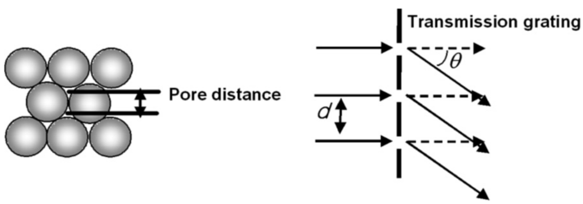


FIGURE 4 UV transmission spectra of (a) 3-dimentional structure fabricated with 480 nm sized silica particles and (b) 2-dimentional structure fabricated with silica particles of 480 nm (solid line) and 560 nm (dashed line).

respectively. The value of ϕ is 0 because most of light is perpendicularly applied to samples. Using these values, λ_{max} of colloidal crystals prepared with 480 nm and 560 nm sized silica particles was calculated to 1056 nm and 1390 nm.

The theoretical value of λ_{max} of 3-dimentional colloidal crystal prepared with 480 nm-sized silica particles was calculated at 1056 nm and the experimental value was measured at 927 nm as shown in Figure 4(a). The difference between theoretical and experimental values might result from the defects and disordered area in the colloidal crystal. 2-Dimentional colloidal crystal showed different optical properties compared to 3-dimentional one as shown in Figure 4(b). The theoretical values of λ_{max} of colloidal crystals prepared with 560 nm and 480 nm sized silica particles calculated using equation (1) were of 1390 nm and 1056 nm and the experimental values were of 617 nm and 537 nm, respectively. Due to the difference experimental and theoretical values, equation (1) could not be applied to the case of 2-dimentional colloidal crystals. To solve this problem, we measured the distance between pores existing among neighboring three particles as follows:



In the case of 2-dimentional colloidal crystals, a pore of 2-dimentional colloidal crystals can regard as a gap of the transmission grating, which was described above scheme. Therefore, the case of 2-dimentional colloidal crystals was applied to Bragg's law of the transmission grating. The average pore distance of 560 nm and 480 nm were measured to be 310 nm and 260 nm, respectively. The theoretical values of maximum diffraction colors of 2-dimentionally built with 560 nm and 480 nm sized silica particles using Bragg's law ($\lambda_{max} = 2d\sin\phi$) were calculated to be 620 nm and 520 nm, respectively, and these values were consistent with the experimental values of 617 nm and 537 nm. It is presumed that the deviation between these values was also caused by array defects.

CONCLUSION

Uniformly sized silica spherical particles were prepared using TEOS under basic catalyst condition by sol-gel method. Two kinds of colloidal crystals, 3-dimentional and 2-dimentional structure, were fabricated using these silica particles by solvent evaporation method. The assembled shapes were confirmed with SEM photograph and optical properties were measured by UV transmission spectroscopy. In the case of 3-dimentional structure, colloidal crystal showed FCC structure and photonic band gap, which was considerably dependent of particle size. On the other hand, in the case of 2-dimentional monolayer structure, they showed hexagonal structure and stop band related to air gap distance located in neighboring three particles.

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