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Tunable Structural Color in Colloidal Crystal Films

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A new class of colloidal crystals has been fabricated whose structural color could be tuned by changing the lattice constants. The crystals were composed of polystyrene (PS) microbeads embedded in a silicone elastomer matrix. The PS microbeads were self-assembled as cubic-close packing, ccp, on hydrophilic substrates by a new method. The ccp(111) planes parallel to the substrate cause the structural color of the crystal film due to the Bragg's diffraction of incident light. The center-to-center distance between the PS beads could be tuned by swelling the silicone elastomer with organic solvents. In addition, the swelling time is less than 0.4s for the composite film having 50 μm thickness. The tuning structural color can change a wide range on visible light wavelength. A composite film assembled with 175nm PS microbeads exhibit a violet color having a stop band at 448 nm (initial). The structural color changed green (524 nm) for iso-propanol and red (714 nm) for hexane. When the composite film was pulled out the solvent and dried in air, the structural color of the swollen film returned to the initial color. There was no rupture on the composite film after 30 times of the cycle of swelling and shrinking. The present work offers a new three-dimensional photonic crystal with tunable and reversible stop band on a wide range of visible light.

Key words: Colloidal Crystal, Bragg' Diffraction, Structural Color, Swelling, PDMS Gel

1. INTRODUCTION

Colloidal crystals are three-dimensionally periodic lattices of mono-dispersed, spherical colloids such as polymer beads and silica colloids [1]. The periodic lattices of the colloidal, d, crystal will diffract the incident light in accordance with the following Bragg's law. λ and n represents wavelength of the reflected light and refractive index of the colloidal crystal, respectively.

$$\lambda = 2dn \qquad (1)$$

The reflected light is well kwon as structural color [2].

Tuning the structural color enable use for an optical sensor without using special detector equipment. Asher et al. fabricated a hydrogel colloidal crystal, which can detect changing temperature-, pH-, and ion-concentration [3]. In the hydrogel, the lattice distance varied in response to the environmental change(s), and in some cases, such a variation could be readily picked up by naked eyes. The colloidal crystal embedded in hydrogels can serve as mechanical sensors for measuring strains applied through by one-dimensional stretching or compressing [4]. Furthermore, swelling and shrinking of periodic structure of hydrogels have been working for their technological applications [5]. Most recently, two research groups demonstrated a new application for new type of display media [6].

This paper demonstrates a tunable structural color of the colloidal crystal films embedded in silicone elastomer (gel). Figure 1 shows a principle of the tuning structural color by swollen with a silicone liquid or an organic solvent. A colloidal crystal of polystyrene, PS, beads is filled with polydimethylsilicone, PDMS, elastomer. The lattice distance, d_1 will expand to d_2 by swelling PDMS matrix. The lattice distance will return to the initial as completely shrunk PDMS matrix. The structural color will change by tuning the lattice distance of d shown in eq. 1.

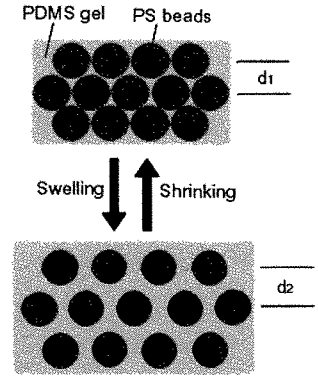

Figure 1: Mechanism of the reversible tuning structural color of the colloidal crystal. Cubic-close packed PS beads are embedded in silicone (PDMS) elastomer matrix. The swelling and shrinking the PDMS matrix reversibly will change lattice distance of the colloidal crystal.

2. Materials and Methods

Mono-dispersed polystyrene (PS) beads were obtained as aqueous dispersions from Polysciences. Silicone liquids with viscosities in the range of 0.65-50 cSt were purchased from Gelest. Polypoly-dimethylsiloxane (PDMS) was obtained from Dow Corning (Sylgard 184). Figure 2 shows a flow of the preparing composite films of crystallized PS beads embedded in PDMS matrix. The surfaces of glass were made hydrophilic by treating with oxygen plasma. The colloidal crystals (in the form of thin films) were fabricated by drying the aqueous dispersion of PS beads on glass substrates. In a typical procedure, ~0.5 mL of the PS dispersion was placed on a piece of glass slide (25 mm x 25 mm) to form a thin layer of liquid film. The surface of this liquid film was then completely covered with a silicone liquid (DMS-T11, 10 cSt). PS beads were crystallized at room temperature for a few days. After crystallization, the voids among crystallized PS beads were infiltrated with the premixed, PDMS precursor. Then the PDMS elastomer was cured for 24 hours in room temperature and then 6 hours at 55 ℃.

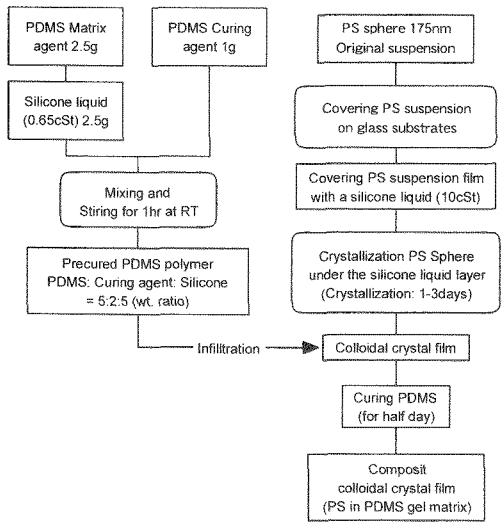

Figure 2. Experimental flow for preparing PS colloidal crystal film embedded in PDMS gel composite.

3. Results and Discussion

Figure 3 shows SEM images of the composite film. The upper and lower photos show the surface and cross section images, respectively. The surface image indicates hexagonal packing with line defects of triangle shapes. The cross sectional image indicates other hexagonal packing and cubic packing planes. These SEM images support that the crystallized PS beads are cubic close packing (ccp) and ccp (111) planes are parallel to the substrate. Therefore the structural color of the composite film is caused by Bragg's diffraction of the incident light from the planes of ccp (111).

Figure 4 shows the UV-Vis spectrometer of the composite film consisting of 202 nm PS beads from (violet color) to near-IR wavelength. The dip position of the original film, 550 nm is shifted to 725 nm as immersed in a silicone liquid (DMS-T00). The structural color immediately changed from green color to red color due to swelling the composite film. Then the film pulled out from the DMS-T00 and completely dried in air. The dip position returned to the original position due to the shrinking of the PDMS matrix. This swelling and shrinking of the composite film is completely reversible and repeatable over 30 times. There was no rupture on the composite film.

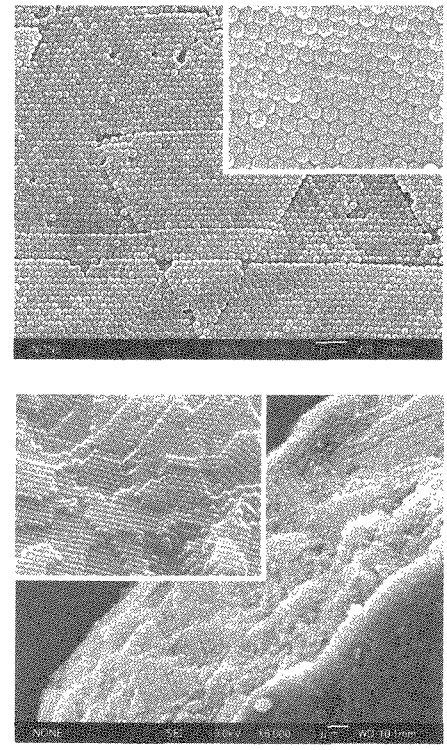

Figure3. SEM images of the colloidal crystal film assembled with 202 nm PS beads embedded in silicone elastomer matrix. Upper: Surface image of the film having hexagonal packing plane. Lower: Cross sectional image. The enlarged image indicates hexagonal and tetragonal packing planes.

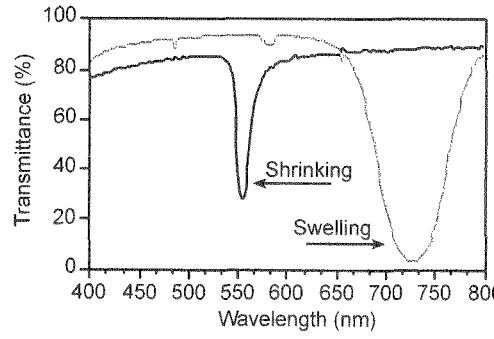

Figure 4. Changing structural color by swelling and shrinking of the colloidal crystal film. The composite film consists of 202 nm PS beads and PDMS matrix indicates green on initial and red on swollen using volatile silicone liquid. This tuning is completely reversible and repeatable.

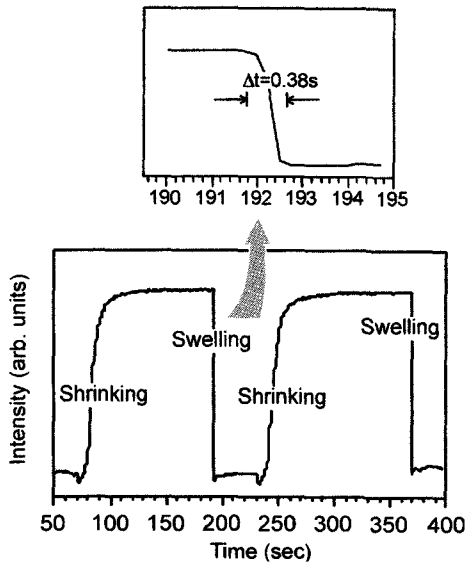

Figure 5. Reflected light intensity at 550 nm, initial dip position, as a function of time. Repetition of swelling and shrinking of the composite film of 202 nm PS beads.

Figure 5 shows the repetition of the swelling and shrinking of the composite of 50 μm film thickness. The reflected light intensity at 550 nm decreased immediately as covering a drop of the DMS-T00. The swelling of the composite film was completed within 0.4 seconds. Tuning structural color was high response rate comparing with colloidal crystal composite embedded in hydrogels. In contrast, shrinking time is longer than swelling time. For the shrinking the composite film, it took over 30 seconds. The reflected light intensity recovered the same level after the treatment of swelling and shrinking. This result also supports that the composite film was completely reversible.

Shift of the dip position was almost cover visible light wavelength (400 – 750 nm) using 175 nm PS beads. Figure 6 shows tuning dip position from 448 nm as initial, 524 nm in isopropyl alcohol and 714 nm in hexanes. The composite film changed its structural color from violet, green to red.

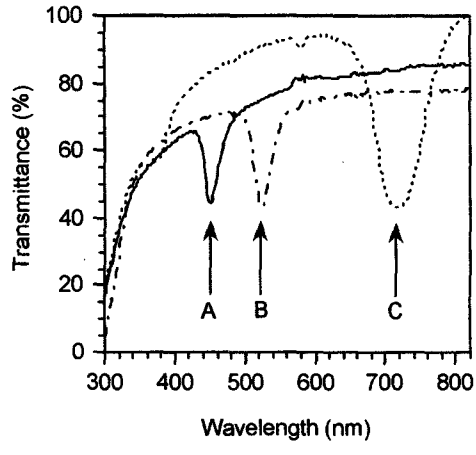

Figure 6. Tuning Structural Color from Violet to Red in visible wavelength. A: Initial position of the film (175nm PS colloidal crystal composite), B: in isopropyl alcohol, C: in Hexanes

Fig. 6 shows that the structural color depends on the solvent type. Therefore, this composite film has a potential application for a new chemical sensor using structural color. Since one can recognize the solvent judged by naked eye. Tuning color is one of the important advantages for convenient and simple examination. An application of tuning structural color is commercial as a thermo-sensor using liquid crystal film. Like this application, the developed composite film can be applied to a chemical sensing for solvents without use of detecting equipment.

4. Conclusion

This paper reported the new colloidal crystal film with reversibly tunable structural color. The expanding lattice in the colloidal crystal film caused this tuning the color. The film is completely reversible and repeatedly usable for the cycle of swelling and shrinking over 30 times. Tuning structural color almost visible light region from violet to red. The composite films offer a new three-dimensional photonic crystal with tunable and reversible stop band on a wide range of visible light.

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