Tuning and fixing of uniform Bragg reflection color of gel-immobilized colloidal photonic crystal films

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ABSTRACT

We demonstrate the facile tuning of uniform Bragg reflection color from red to blue by uniaxial compression of gel films containing single-crystalline loosely packed colloidal crystals. The tuned colors can be fixed by photopolymerization of a polymer precursor solution contained in the compressed gel films.

Colloidal crystals are three-dimensional periodic arrays of monodisperse particles that provide a simple and efficient way to create three-dimensional photonic crystals.[1-4] Colloidal crystals exhibit a bright reflection color due to Bragg reflection at the optical stopband wavelength and are expected to perform well as reflective color pigments that do not degrade under ultraviolet (UV) light. In particular, colloidal crystals with a low particle volume fraction immobilized in a polymer gel have attracted considerable attention due to their tunable optical properties.[5-7] The volume of the gel can be varied by applying an external stimulus (e.g., change in pH,[8] temperature,[9] or solvent[10]), which changes the lattice spacing of the colloidal crystals immobilized in the gel. Thus, the optical stopband wavelength or Bragg reflection color can be altered on demand. These features are expected to be used for tunable photonic crystals, lasers,[11] filters,[12] and chemical and biological sensors.[13,14] Uniaxial mechanical compression is a facile tuning method[12,15] wherein a gel-immobilized colloidal crystal is placed between two glass substrates and compressed to reduce the lattice spacing oriented vertical to the substrate surface. The Bragg wavelength can be readily altered according to the degree of compression. When the compression is released, the Bragg wavelength returns to its initial value; therefore,

reversible and repeatable tuning is possible. However, to maintain the adjusted Bragg wavelength, constant compression is needed. In addition, evaporation of the swelling solvent alters the Bragg wavelength. The low stability of colloidal crystals suggests that their applications are currently limited.[12] Furthermore, although gel-immobilized colloidal crystals with a low particle volume fraction have the advantage of Bragg wavelength tuning over a wide wavelength range because of their large interparticle separation, common preparation methods provide polycrystalline structures with low optical quality.[15] Therefore, tuning a uniform Bragg reflection color over a sample area is difficult, although it is essential for practical applications.

In this study, we demonstrate the facile tuning of uniform Bragg reflection color by uniaxial compression of gel films containing single-crystalline loosely packed colloidal crystals processed under shear flow. Color tuning from red to blue was achieved according to the degree of compression while maintaining color uniformity. In addition, we show that the tuned Bragg reflection colors can be fixed by the photopolymerization of a polymer precursor solution contained in the compressed gel films. Thus, solvent-free polymer films with uniform colors, such as red, green, and blue, were obtained using one type of gel film by changing the degree of compression.

We used gel films containing single-crystalline loosely packed colloidal crystals processed under shear flow. The detailed preparation method has been described previously.[16] Briefly, a suspension of monodisperse polystyrene particles (Thermo Scientific, particle diameter of 160 nm) was mixed with an ion-exchange resin (Bio-Rad, AG501-X8(D)) for deionization. Gelation reagents —*N*-isopropylacrylamide (NIPAM) and *N*-methylolacrylamide (NMAM) as monomers, *N*,*N'*-methylenebisacrylamide (BIS) as a cross-linker, and 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA) as a photoinitiator—and ultrapure water (Millipore, Milli-Q system) were added to the suspension so that the NIPAM, NMAM, BIS, VA, and particle concentrations were 400 mM, 400 mM, 40 mM, 0.35 mM, and 12.0 vol%, respectively. The suspension was shear-flowed into a flat capillary cell (channel height: 0.1 mm; width: 9 mm; length: 70 mm) to obtain a single-domain crystal.[17,18] The flow-aligned particle array was then immobilized in the gel network by photopolymerizing the gelation reagents under UV light (MORITEX SCHOTT, MBRL-CUV7530). The obtained gel film containing loosely packed single-crystalline colloidal crystals was cut into discs with a diameter of 3 mm and immersed in a hydrophilic polymer precursor solution of 4-hydroxybutyl acrylate (HBA) with 1 wt.% photoinitiator (BASF Japan Ltd., DAROCUR 1173) for approximately 24 h to replace the water contained in the gel film with the precursor solution.

The gel film was then placed between two parallel quartz substrates inside a mechanical compression apparatus and compressed uniaxially using three micrometers (Fig. 1). In this system, the distance between the parallel substrates was adjusted reversibly with an accuracy of ± 0.2 μm, owing to the use of micrometers and springs. Photographs of the films for varying distance between the substrates were taken from above using a charge-coupled device (CCD) camera (Sony, XCD-V60CR),

and reflection spectra were recorded using a multichannel spectrometer (Soma Optics, Fastevert S-2630).

Figure 2A shows photographs of the film under different degrees of compression. As the distance between substrates was decreased from 96 μm to 70 μm, the area of the film gradually increased due to compression, and the reflection color changed from red to blue while retaining excellent uniformity over the sample area. The film at a substrate distance of 96 μm (i.e., before compression) exhibited a strong peak at 665 nm in the reflection spectrum (Fig. 2B). The peak was identified as Bragg reflection from the (111) lattice planes of the face-centered cubic (FCC) structure parallel to the film surface from consideration of the Bragg condition at normal incidence:[19]

$$\lambda_{hkl} = 2n_{\mathrm{c}}d_{hkl}, \qquad (1)$$

where λ_{hkl} and d_{hkl} are the Bragg wavelength and lattice spacing of the (*hkl*) planes, respectively. n_{c} is the refractive index of the colloidal crystals, which can be approximated as the volume-weighted average of the refractive indices of the components of the gel-immobilized colloidal crystal film:[7]

$$n_{\mathrm{c}} = n_{\mathrm{p}}\phi_{\mathrm{p}} + n_{\mathrm{pol}}\phi_{\mathrm{pol}} + n_{\mathrm{sol}}\big(1 - (\phi_{\mathrm{p}} + \phi_{\mathrm{pol}})\big), \qquad (2)$$

where n_{p}, n_{pol}, and n_{sol} are the refractive indices of the particles (1.59), polymer in the gel (1.43), and precursor solution (1.45), respectively. ϕ_{p} and ϕ_{pol} are the volume fractions of the particles and polymer in the gel film, respectively. The relation between ϕ_{p} and ϕ_{pol} was determined from the masses of the gelation reagent and particles added into the suspension: $\phi_{\mathrm{pol}} = 0.74\ \phi_{\mathrm{p}}$.[7] From geometrical considerations, the lattice spacing of the FCC (111) planes, d_{111}, is determined using ϕ_{p} and the diameter of the colloidal particles, d:

$$d_{111} = \left(\frac{2\pi}{9\sqrt{3}\phi_{\mathrm{p}}}\right)^{\frac{1}{3}} d. \qquad (3)$$

As the distance between the substrates decreased from 96 μm to 70 μm, the Bragg wavelength blueshifted linearly from 665 nm to 496 nm while preserving the excellent spectral profile (Figs. 2B and C). When the compression was released, the Bragg wavelength returned to its initial value of 665 nm. The linear and reversible tuning over a wide wavelength range is due to the large interparticle separation of colloidal crystals with a low particle volume fraction immobilized in the gel film. This is advantageous for tunable photonic crystals in practical applications. In this system, fine tuning of the Bragg wavelength (3 nm) was possible, with a minimum variation of the distance between substrates of 0.5 μm, as shown in the inset of Fig. 2C.

The shift of the Bragg wavelength by compression can be quantitatively explained by the changes in the lattice spacing vertical to the film surface and the refractive index of the colloidal crystals using Bragg's law. Assuming that the rate of change in the lattice spacing vertical to the film surface is equal to the rate of change in the distance between the substrates, the lattice spacing under compression d_{hkl}^{c} is given using the distance between the substrates under compression D^{c}, the distance between the substrates immediately before compression D^{i}, and the lattice spacing before compression, d_{111}:

$$d_{hkl}^{c} = \left(\frac{D^{c}}{D^{i}}\right) d_{111}. \qquad (4)$$

In addition, the particle volume fraction of the film under compression ϕ_p^c is calculated using the volume of the film immediately before compression V^i, the volume of the film under compression V^c, and the particle volume fraction immediately before compression ϕ_p^i:

$$\phi_p^c = \left(\frac{V^i}{V^c}\right) \phi_p^i. \qquad (5)$$

The volume of the film was calculated by multiplying the film area observed through the CCD camera by the distance between the substrates. By substituting the estimated d_{hkl}^c and ϕ_p^c values into Eqs. 1 and 2, the Bragg wavelengths for the film under compression were estimated and are shown as a solid line in Fig. 2C. The calculated Bragg wavelengths are in reasonable agreement with the observed wavelengths.

The tuned Bragg wavelength can be fixed by polymerization of the precursor solution contained in the compressed gel film. For example, a gel film exhibiting a blue color at a distance of 70 μm between the substrates was irradiated with UV light for 10 min, and the precursor solution was solidified to fix the particle array. As shown in Fig. 3A, a uniform blue color was maintained even after removal from the substrates, although the Bragg peak became slightly broad. Similarly, solvent-free polymer films of various colors, such as green and red, were obtained by photopolymerization of one kind of gel film by changing the degree of compression, as shown in Figs. 3B and C, respectively. The Bragg wavelength was slightly blueshifted after photopolymerization. This was explained by the slight shrinkage of the film observed using the CCD camera and the change in the refractive index during the conversion from the precursor solution to the polymer.

In summary, we succeeded in the facile tuning of uniform Bragg reflection color by uniaxial compression of gel films containing single-crystalline loosely packed colloidal crystals processed under shear flow. Color tuning from red to blue was achieved according to the degree of compression while maintaining uniformity. The Bragg wavelength could be tuned linearly and reversibly over a wide wavelength range (496 - 665 nm) owing to the large interparticle separation. In this system, a fine tuning resolution of 3 nm was possible, with a smallest variation in the distance between the substrates of 0.5 μm. Furthermore, the tuned Bragg reflection color could be fixed by the photopolymerization of a polymer precursor solution contained in the compressed gel film. Thus, solvent-free polymer films with uniform colors, such as red, green, and blue, were obtained using one type of gel film by changing the degree of compression.

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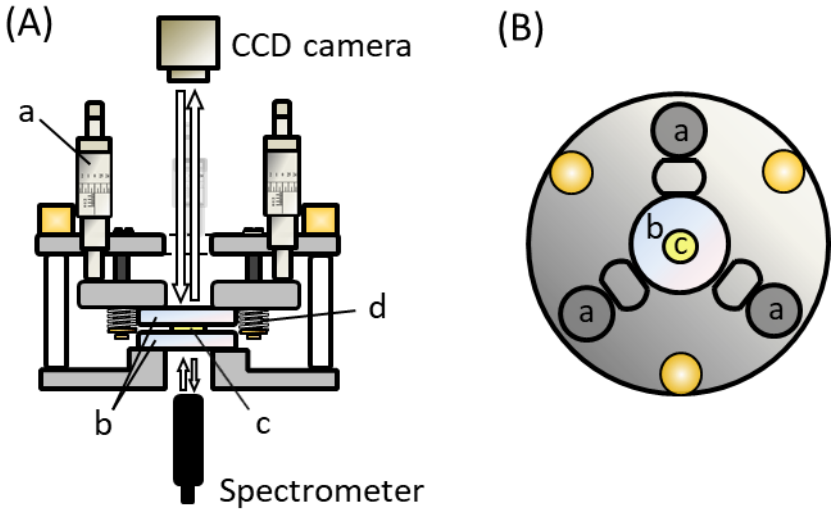

Fig. 1 Schematic diagram of the mechanical compression apparatus used for tuning the Bragg wavelength of the gel-immobilized colloidal crystal film. (A) Side view and (B) top view (a: micrometer, b: quartz substrate, c: gel film, d: spring).

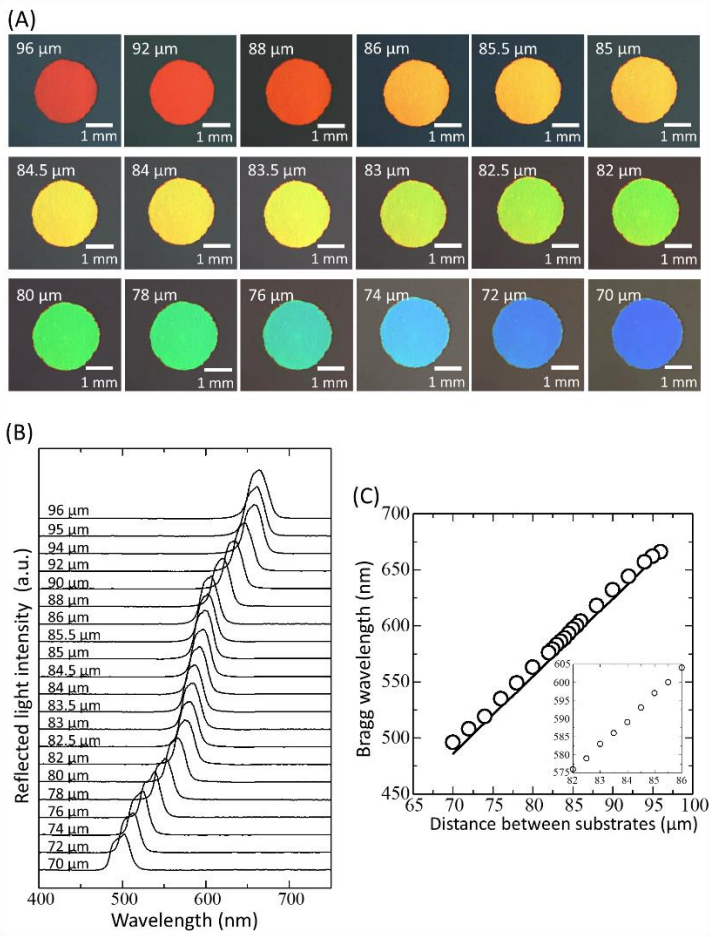

Fig. 2 (A) Photographs and (B) reflection spectra for the gel-immobilized colloidal crystal film at various distances between the substrates. (C) Plot of the Bragg wavelength as a function of the distance between the substrates. The solid line is a calculated curve. The inset represents the enlarged graph.

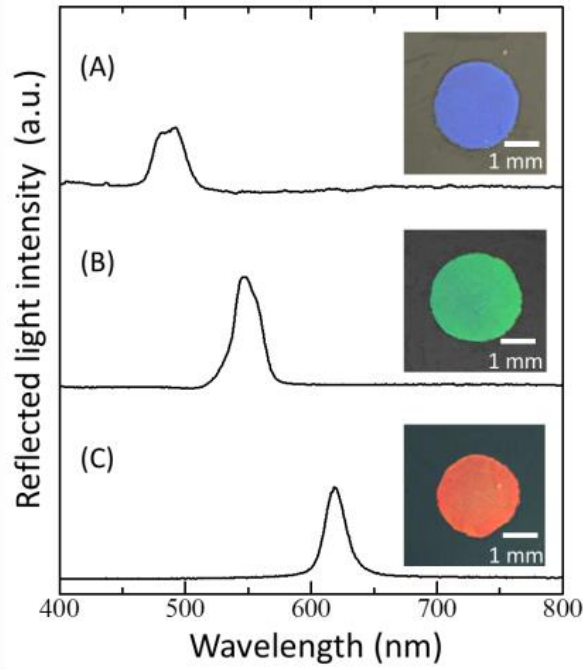

Fig. 3 Reflection spectra and photographs of the solvent-free polymer films containing colloidal crystals prepared at different distances between substrates of (A) 70 μm, (B) 82 μm, and (C) 92 μm.