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Wide Spectral Tuning of Gel-immobilized Colloidal Crystals Preserving High Uniformity

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We evaluated the spectral uniformity of a widely tunable gel-immobilized colloidal crystal film containing an ionic liquid. Transmission spectral characterization by imaging spectroscopy indicated that the film preserved high uniformity over the entire sample area, in spite of the great volume change during tuning. The standard deviation of the transmittance and Bragg diffraction wavelength of the film were less than 7% and 5 nm, respectively.

Gel-immobilized colloidal crystals are three-dimensional periodic arrays of monodisperse colloidal particles immobilized in a gel network.[1] The spatial periodicity of the refractive index between the particle arrays and the surrounding gel results in an optical stop band, and hence, the arrays act as photonic crystals in the optical regime.[2] Since the gel matrix undergoes volume changes in response to environmental modifications, such as changes in solvent, temperature, or pH, the optical stop band wavelength or Bragg diffraction wavelength for the gel-immobilized colloidal crystals can be tuned by applying external stimuli.[3] Therefore, they are potentially useful as tunable photonic crystals, for applications which include tunable lasers, tunable optical filters, optical switches, and biological and chemical sensors.[4] However, to date, the difficulties of preparing large single crystalline arrays immobilized in a gel network and preventing destruction of the crystalline arrays owing to the evaporation of solvent in the gel has hindered the development of practical applications of tunable colloidal photonic crystals.

We have developed a fabrication method for a large gel film containing single-crystal-like colloidal crystals by the combination of a shear-induced method and a photopolymerization technique:[5,6] a suspension of charged colloids in a polycrystalline state is converted into a single domain in a flat capillary cell by the shear-flow effect.[5] The formed single-domain crystal is subsequently immobilized through photopolymerization of gelation reagents already present in the starting suspension.[6] Furthermore, we have recently found that ionic liquids, which are salts in the liquid state at room temperature,[7] can be used as nonvolatile swelling solvents for the gel-immobilized colloidal crystals.[8] We also found that by varying the mixing ratio of hydrophilic and hydrophobic ionic liquids, the swelling volume of the gel could be significantly changed, resulting in the wide tuning of the lattice constant or Bragg diffraction wavelength of the crystals. Thus, we could fabricate single-crystal-like colloidal photonic crystals having wide tunability in which there is no solvent evaporation. However, the substantial volume change of the gel can potentially generate strain; in this case, the gel may shrink or swell inhomogeneously, leading to deterioration of crystal uniformity. Therefore, the examination of the uniformity of the tuned colloidal crystals is an important step toward optical applications of these materials as tunable photonic crystals.

In this letter, we quantitatively evaluate the spatial uniformity of the widely tunable gel-immobilized colloidal crystal films containing ionic liquids in terms of transmission characteristics using an imaging spectrometer. While reflection measurements have been predominantly used for characterizing colloidal crystals, transmission measurements are more sensitive to disorder owing to the use of light transmitted through the crystals. We measured the spatially resolved transmission spectra of the films at an in-plane image resolution of 50 × 25 microns. The spectral uniformity of the films was evaluated by statistically analyzing the pixel-by-pixel spectra in the sample area and obtaining the average transmission spectra, standard-deviation spectra, single-wavelength images, spatial distributions of the Bragg wavelengths, and standard deviations of the Bragg wavelengths. Surprisingly, we found that the film preserved high spectral uniformity over the entire sample area despite the great volume change of the gel.

The gel-immobilized colloidal crystal films containing ionic liquids were prepared following a previously reported detailed procedure.[5,6,8] A suspension of monodisperse colloidal silica particles (Nippon Shokubai Co., Ltd., KE-W20; particle diameter: 210 nm; CV: 7%) was deionized in vials using mixed-bed ion-exchange resin until the suspension showed iridescence indicative of a crystal phase. This colloidal crystal was mixed with aqueous solutions of a monomer, *N*-methylolacrylamide (N-MAM); a crosslinker, *N*,*N*′-methylenebisacrylamide (BIS); and a photoinduced polymerization initiator for ultraviolet (UV) light, 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA). The mixture was then injected into a flat capillary cell (internal dimensions: 0.1 mm thick, 9 mm wide, and 50 mm long) and processed with a momentary strong shear flow to obtain a single-crystal-like domain extending throughout the capillary. The resultant flow-aligned particle arrays were immobilized by the photopolymerization of the gelation reagents in a UV-light exposure chamber. The prepared large gel film containing the single-crystal-like colloidal crystals was cut into circular fragments with diameters of 3 mm, which were then immersed in ionic liquid mixtures for several days to replace the water in the gel with the ionic liquid. We used mixed solutions of a hydrophilic ionic liquid, 1,3-diallylimidazolium bromide, and a hydrophobic ionic liquid, 1,3-diallylimidazolium bis(trifluoromethanesulfonyl)imide, in various volume fraction ratios to tune the Bragg diffraction wavelength.

Figure 1 shows transmission spectral properties of the gel-immobilized colloidal crystal films containing ionic liquids with different mixing ratios *x* when the incident light is normal to the film face. Figure 1a shows the transmission images of the films with different *x* values. These images qualitatively indicated that

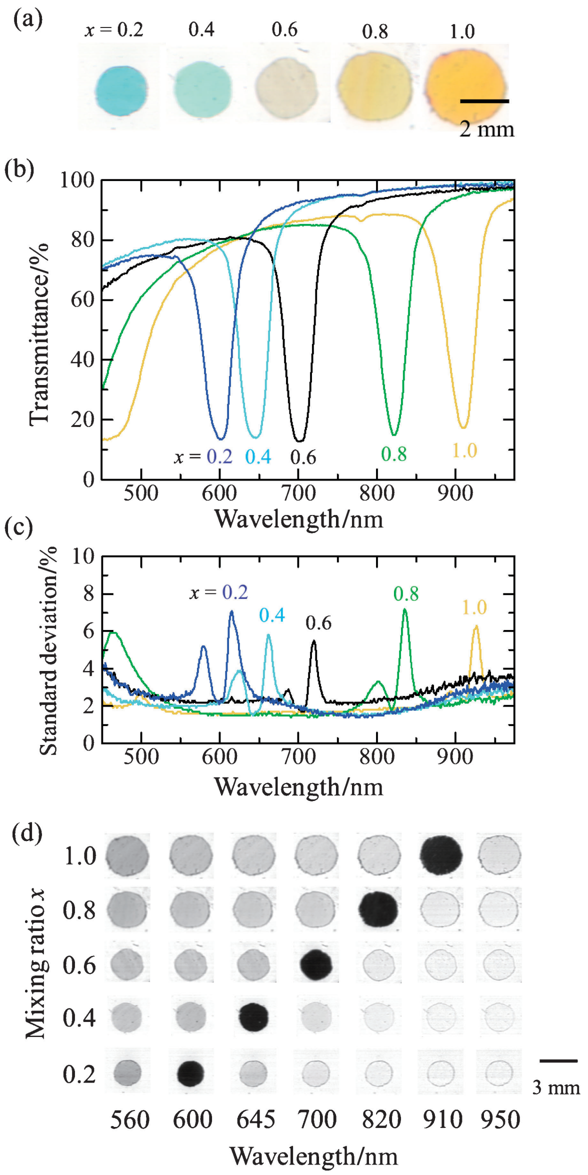

Figure 1. (a) Image of the gel-immobilized colloidal crystal films immersed in mixed solutions of 1,3-diallylimidazolium bromide and 1,3-diallylimidazolium bis(trifluoromethanesulfonyl)imide at various mixing ratios. The parameter x is the volume fraction of 1,3-diallylimidazolium bromide measured prior to mixing. (b) Average transmission spectra of the gel-immobilized colloidal crystal films with different mixing ratios x. The dark level of the transmittance increases by a few percent due to the characteristics of the charge-coupled-device spectrometer. (c) Standard-deviation spectra of the gel-immobilized colloidal crystal films with different mixing ratios x. (d) Single-wavelength images of the gel-immobilized colloidal crystal films with different mixing ratios x for representative wavelengths taken under transmission illumination.

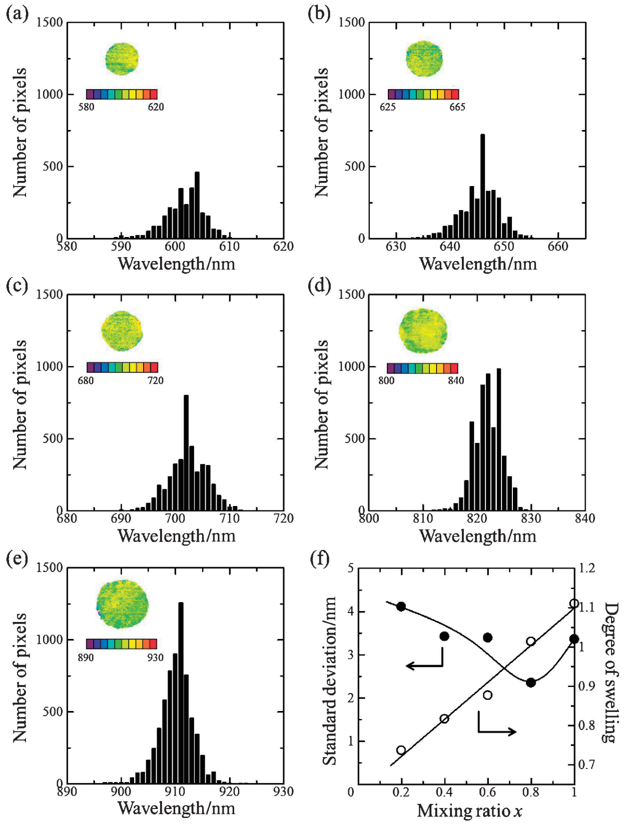

Figure 2. The numbers of the pixels at particular Bragg wavelengths for the gel-immobilized colloidal crystal film with mixing ratios of (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$, (d) $x = 0.8$, and (e) $x = 1.0$. The inset shows the spatial distribution image of the Bragg wavelength. (f) Standard deviation of the Bragg wavelength and degree of swelling of the gel-immobilized colloidal crystal films as a function of the mixing ratio x.

the films were uniform with different color dependent on the swelling size. The average spectrum of the film indicated that all films had high crystalline quality; a deep dip due to an optical stop band caused by the Bragg diffraction from the (111) lattice planes of the face-centered-cubic (FCC) structure and a high transmittance at the pass-band wavelength were observed (Figure 1b). Upon decreasing the mixing ratio x, the dip in the spectrum shifted significantly to shorter wavelengths because of the decrease in the lattice constant of the crystals; the dip wavelength decreased in the wavelength range from about 900 to 600 nm on decreasing the mixing ratio from $x = 1.0$ to 0.2. The uniformity of the widely tunable colloidal crystal film was quantitatively evaluated from the standard deviation of the transmittance, i.e., the standard-deviation spectrum, which was calculated from the pixel-by-pixel spectra for the entire sample area (Figure 1c). For all films, the values of the standard deviation of the transmittance at the pass-band wavelength, which reflect the single-crystalline quality,[9] were as small as 4%. Even though the values increased at the both sides of the dip, they were still as small as 7%. These results quantitatively indicate that the films maintain the spatial uniformity of the transmittance after tuning. The uniformity of the films was also confirmed visually in the spatial distribution of the transmittance with brightness at the representative wavelengths as shown in Figure 1d. Although the absence of uniformity in the transmittance is detected on the basis of the contrast in brightness,[9] these images show uniform texture with black color at the stop-band wavelength and uniform textures with white or gray color at the pass-band wavelengths.

We also evaluated the spatial uniformity of the Bragg diffraction wavelength for the same films from the numbers of the pixels at particular Bragg wavelengths, i.e., histograms of the Bragg wavelength, spatial distribution images of the Bragg wavelength, and standard deviations of the Bragg wavelength (Figure 2). These data indicated that all films had excellent uniformity in terms of the Bragg wavelength. The most contracted film with $x = 0.2$ showed the largest standard deviation value, but it was still less than 5 nm (Figure 2f). Thus, the gel-immobilized colloidal crystal films having wide tunability maintained high spectral uniformity.

In summary, we have quantitatively demonstrated for the first time that gel-immobilized colloidal crystal films containing ionic liquids preserve high transmission spectral uniformity in spite of the great volume change. The widely tunable high-quality colloidal crystals containing nonvolatile ionic liquids have great potential as practical materials for tunable photonic crystals.

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