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Swelling of Gel-Immobilized Colloidal Photonic Crystals in Ionic Liquids

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Supporting Information

Gel-immobilized colloidal crystals are a three-dimensional periodic structure of monodisperse particles immobilized in the gel network.[1] The spatial periodicity of the refractive index of the colloidal crystals results in an optical stop band, and hence, they act as photonic crystals in the optical regime.[2] The gel-immobilized colloidal crystals consist of three components, i.e., particles, gel-network materials, and solvents. Various functional particles such as magnets and semiconductors have been prepared, and novel photonic crystals with special functionalities have been developed with these particles.[3] Further, various stimuli-sensitive gels, which undergo a volume change in response to external stimuli such as changes in temperature and pH, have been used.[4] The lattice constant or optical stop band of the colloidal crystals embedded in these gels can be altered on demand by applying external stimuli; this is useful for applications such as tunable photonic crystals[5] and biological and chemical sensors.[6] On the other hand, to the best of our knowledge, approaches for preparing solvents other than aqueous solutions have not been explored, except for polyhydric alcohols[7] and poly(ethylene glycol) derivatives.[8] Since most organic solvents have a weak affinity for hydrogels, the gels shrink greatly in organic solvents, resulting in the destruction of the crystallinity of the colloids immobilized in the gel. In addition, the evaporation of the solvent can also destabilize these gel-immobilized colloidal crystals.

Recently, ionic liquids, which are salts in the liquid state at room temperature, have received increasing attention as new solvents.[9] They have many attractive features such as nonvolatility, noncombustibility, high ionic conductivity, high thermal stability, and favorable solvating properties; moreover, ionic liquids have the potential for use in fuel cells (as a nonvolatile electrolyte),[10] gas handling,[11] and cellulose processing.[12] The properties of ionic liquids can be adjusted by changing the cation−anion combination. Thus, the use of ionic liquids as solvents for gel-immobilized colloidal crystals will increase the possibility of designing colloidal photonic crystals in which there is no solvent evaporation. In this Communication, we show that hydrophilic ionic liquids can be used as suitable swelling solvents for gel-immobilized colloidal crystals. The optical stop band of the colloidal crystals can be adjusted over a wide range of wavelengths by varying the mixing ratio of hydrophilic and hydrophobic ionic liquids; the stop-band wavelength is linearly dependent on the mixing ratio, which is quite advantageous in practical applications.

Our system consists of loosely packed colloidal crystals immobilized in a hydrogel film. The detailed preparation method for the gel-immobilized colloidal crystal films is described in the Supporting Information. An aqueous suspension of charged silica or polystyrene particles (diameter: $\sim 0.2\,\mu$m) in a crystalline state was converted into a single-crystal-like structure in a flat flow cell by using the shear-flow effect.[13] The single-domain crystal was immobilized through the photopolymerization of gelation reagents (*N*-methylolacrylamide as a monomer, *N*,*N*′-methylenebis(acrylamide) as a cross-linker, and a polymerization initiator) that had been added to the starting suspension in advance.[14] Thus, we obtained a self-standing gel film containing the loosely packed colloidal crystals (about 10% in particle volume fraction); the film was cut into circular fragments with a diameter of 3 mm. The circular fragments were soaked in an ionic liquid for a few days to replace the water in the gel with the ionic liquid.

When a gel film is soaked in hydrophobic ionic liquids such as 1,3-diallylimidazolium bis(trifluoromethanesulfonyl)imide, the gel shrinks considerably, as is the case with most organic solvents. In such a case, the structure of the colloidal crystal immobilized in the gel is destroyed; the sample turns cloudy, and the Bragg peak in the spectrum disappears. On the other hand, after soaking the gel film in hydrophilic ionic liquids, the crystalline structure of the colloids remains intact. The swelling volume of the gel-immobilized colloidal crystals varies with the type of ionic liquid (Table S1 in Supporting Information). In some hydrophilic ionic liquids, the gel film swells to an extent greater than that in water, as shown by the reflection spectra and microscope images before and after replacing water with 1,3-diallylimidazolium bromide in Figure 1. The film swells to 1.04 times its initial size when water is replaced with the ionic liquid, leading to a different diffraction color or red shift of the reflection peak in the spectrum. For the film immersed in water, a strong reflection peak is observed at 807 nm, which is due to Bragg diffraction from the (111) lattice planes of a face-centered-cubic (FCC) structure parallel to the cell surface. When the ionic liquid replaces the water, the peak shifts to a longer wavelength of 956 nm, maintaining high spectral quality. The red shift of the Bragg wavelength can be explained by the increase in the lattice spacing and refractive index of the crystals immobilized in the gel.

The Bragg diffraction wavelength from FCC (111) lattice planes in the case of normal incidence is given by

$$\lambda_{111} = 2n_c d_{111} \qquad (1)$$

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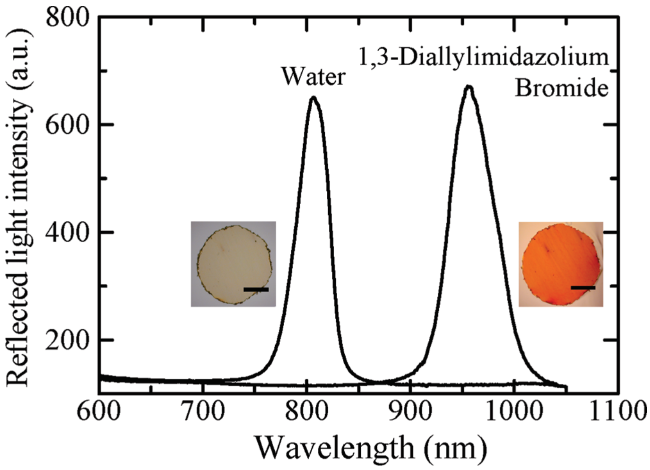

Figure 1. Reflection spectra and microscope images of gel-immobilized silica colloidal crystal film before and after the replacement of water in the gel with 1,3-diallylimidazolium bromide. The length of the scale bars is 1 mm.

where n_c is the refractive index of the colloidal crystals and d_{111} is the interplanar spacing of (111) lattice planes. The value of d_{111} in the case of the FCC structure can be estimated from geometrical considerations by using the particle volume fraction ϕ_p and the particle diameter d, and it is given by

$$d_{111} = \left(\frac{2\pi}{9\sqrt{3}}\frac{1}{\phi_p}\right)^{1/3} d \tag{2}$$

The value of n_c can be approximated by a volume-weighted average of the refractive indices of the components:[15]

$$n_c = n_p\phi_p + n_{\text{gel-network}}\phi_{\text{gel-network}} + n_{\text{solvent}}(1 - (\phi_p + \phi_{\text{gel-network}})) \tag{3}$$

where n_p, $n_{\text{gel-network}}$, and n_{solvent} are the refractive indices of the particle, gel-network material, and solvent, respectively. $\phi_{\text{gel-network}}$ is the volume fraction of the gel-network material ($\phi_{\text{gel-network}} = 0.56\phi_p$, which is determined from the masses of the gelation reagent and particles added to the suspension). By substituting the observed peak wavelength for the film immersed in water (λ^0_{111} = 807 nm), the particle diameter (d = 210 nm), and the refractive indices of the components (n_p = 1.45 (silica), $n_{\text{gel-network}}$ = 1.41,[16] and n_{solvent} = 1.33 (water)) in eqs 1−3, the lattice spacing of (111) for the film immersed in water can be calculated to be d^0_{111} = 298 nm. Assuming that the lattice spacing increases to 1.04 times its initial value after the replacement of water with the ionic liquid, the Bragg wavelength for the crystals in the ionic liquid can be estimated by substituting the assumed lattice spacing (d_{111} = 310 nm) and the refractive index of the ionic liquid measured with an Abbe refractometer (n_{solvent} = 1.56) in eqs 1−3. The estimated Bragg wavelength (λ_{111} = 967 nm) is in good agreement with the observed wavelength (956 nm). For the conventional gel-immobilized colloidal crystals immersed in aqueous solutions, the tuning of the optical stop band is restricted to a wavelength region shorter than the Bragg wavelength in the case of water, since the widest lattice spacing is achieved for the crystals immersed in water. On the other hand, we found that even a wider lattice spacing or a longer Bragg wavelength than that in the case of water can be achieved by using hydrophilic ionic liquids as solvents.

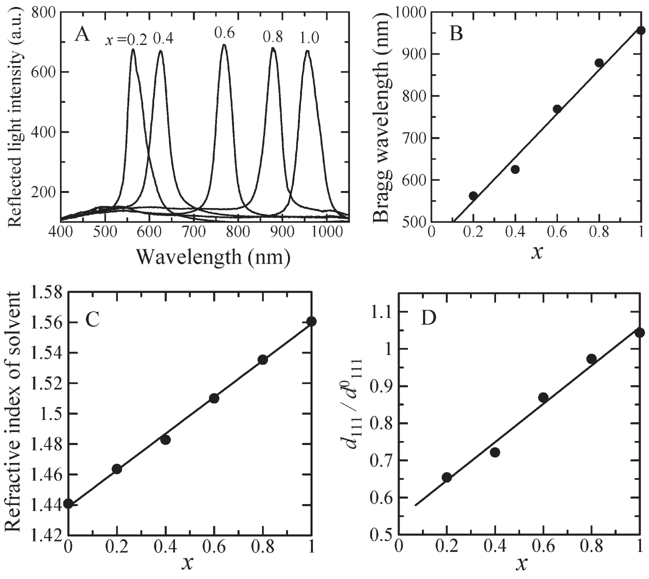

Figure 2. (A) Reflection spectra of gel-immobilized colloidal crystal film immersed in the mixed solution of 1,3-diallylimidazolium bromide and 1,3-diallylimidazolium bis(trifluoromethanesulfonyl)imide for various mixing ratios. The parameter x is the volume fraction of 1,3-diallylimidazolium bromide measured prior to mixing. (B) Bragg wavelength obtained from (A) as a function of x. (C) Refractive index of the solvent, as measured with an Abbe refractometer. (D) Degree of swelling of the gel-immobilized colloidal crystals as a function of the mixing ratio x.

Furthermore, we found that the swelling volume of the gel can be easily varied by adding a hydrophobic ionic liquid (i.e., 1,3-diallylimidazolium bis(trifluoromethanesulfonyl)imide) to the hydrophilic one. Thus, the Bragg wavelength or optical stop-band wavelength of the colloidal crystals can be varied over a wide range. As shown in Figure 2A,B, upon decreasing the volume fraction of the hydrophilic ionic liquid, which is measured prior to mixing, the Bragg reflection peak shifts to a shorter wavelength in a wide range of about 400 nm, preserving the uniform crystalline structure. The value of d_{111} is estimated by using eqs 1−3, the Bragg wavelength (Figure 2B), and the refractive index of the ionic liquid measured with an Abbe refractometer (Figure 2C); the degree of swelling thus obtained (d_{111}/d^0_{111}) is plotted in Figure 2D. These plots are well approximated by a function of the mixing ratio x, i.e., $d_{111}/d^0_{111} = 0.525x + 0.543$, as shown by the solid line in Figure 2D. Surprisingly, the Bragg wavelength and swelling size show linear dependence on the mixing ratio x, which is quite advantageous for adjusting the optical characteristics of the crystals in practical applications. In general, however, the swelling−shrinking phenomenon that depends on the change in the mixing ratio of solvents is known to be a type of phase transition, and the gel size (or Bragg wavelength) is known to be a strongly nonlinear function of the mixing ratio, as already reported for the water−ethanol system.[17] The swelling degree of the gel has been explained with the Flory−Huggins formula by considering the balance of osmotic pressures present interior and exterior of the gel, which is due to the interaction among solvent, gel network, and colloidal particles.[18] While such a nonlinear behavior can be theoretically understood with the formula, the presently observed linear behavior cannot be explained. We speculate

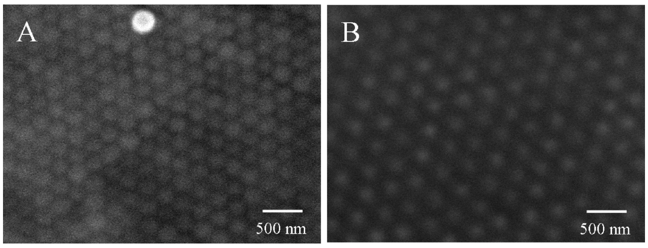

Figure 3. Top-view SEM images of gel-immobilized silica colloidal crystal films with $x = 0.2$ (A) and $x = 0.8$ (B).

that very high concentrations of ions in the ionic liquid might lead to the linear behavior. In addition, it might be necessary to consider the influence of colloidal forces based on Debye–Hückel theory[19] to explain the linear behavior. Theoretical understanding seems to be a challenging work to be done in the future.

Since ionic liquids do not evaporate even in high vacuum, we can directly verify the presence of distance-controlled particle arrays in the swollen gel by using an ordinary scanning electron microscope (SEM) (Figure 3). For $x = 0.2$, relatively dense arrays of silica particles are observed (Figure 3A), while for $x = 0.8$, loose arrays of particles are seen (Figure 3B). This confirms that uniform expansion or shrinkage of the periodic arrays can be successfully attained by changing the mixing ratio of the two different ionic liquids. From the SEM images, the distance between the nearest-neighbor particles, a_0, for $x = 0.2$ and $x = 0.8$ is estimated to be 247 ± 15 and 335 ± 25 nm, respectively. These values are in reasonable agreement with those determined by using the Bragg wavelength. The determination of the values by using the Bragg wavelength is as follows. The a_0 of the FCC structure is given by

$$a_0 = \sqrt{\frac{3}{2}}\, d_{111} \tag{4}$$

By using the observed Bragg wavelength (Figure 2B), refractive index of the solvents (Figure 2C), and eqs 1–4, the distance between the nearest-neighbor particles for $x = 0.2$ and $x = 0.8$ is calculated to be 239 and 355 nm, respectively. This agreement between the values implies that the observed change in the Bragg wavelength results from a change in the periodicity of particle arrays. In addition, the Bragg wavelength is maintained even after taking the sample from the vacuum chamber. The present successful direct observation of the particles immobilized in the hydrogel without evaporation implies that ionic liquids can be used to study wet materials such as gels, tissues, and living cells.

In summary, we have demonstrated that ionic liquids can be used as solvents for gel-immobilized colloidal crystals with high stability and high tunability. Since ionic liquids exhibit good electric conductivity and favorable solvating properties, colloidal photonic crystals containing ionic liquids have potential for use in many new applications, for example, in high-efficiency solar cells, electric-optic conversion materials, and novel functional photonic crystals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedure and characterization data for the gel-immobilized colloidal crystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Kamenetzky, E. A.; Magliocco, L. G.; Panzer, H. P. *Science* **1994**, *263*, 207. (b) Foulger, S. H.; Jiang, P.; Lattam, A.; Smith, D. W.; Ballato, J.; Dausch, D. E.; Grego, S.; Stoner, B. R. *Adv. Mater.* **2003**, *15*, 685.

(2) (a) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059. (b) John, S. *Phys. Rev. Lett.* **1987**, *58*, 2486. (c) Special Issue on Photonic Crystals. *Adv. Mater.* **2001**, *13*, 369. (d) Furumi, S.; Fudouzi, H.; Sawada, T. *Laser Photon. Rev.* **2010**, *4*, 205.

(3) (a) Xu, X.; Majetich, S. A.; Asher, S. A. *J. Am. Chem. Soc.* **2002**, *124*, 13864. (b) Velikov, K. P.; Moroz, A.; van Blaaderen, A. *Appl. Phys. Lett.* **2002**, *80*, 49.

(4) Kanai, T.; Lee, D.; Shum, H. C.; Weitz, D. A. *Small* **2010**, *6*, 807.

(5) (a) Iwayama, Y.; Yamanaka, J.; Takiguchi, Y.; Takasaka, M.; Ito, K.; Shinohara, T.; Sawada, T.; Yonese, M. *Langmuir* **2003**, *19*, 977. (b) Kanai, T.; Sawada, T.; Toyotama, A.; Yamanaka, J.; Kitamura, K. *Langmuir* **2007**, *23*, 3503.

(6) (a) Holtz, J.; Asher, S. A. *Nature* **1997**, *389*, 829. (b) Saito, H.; Takeoka, Y.; Watanabe, M. *Chem. Commun.* **2003**, 2126.

(7) Toyotama, A.; Sawada, T.; Yamanaka, J.; Kitamura, K. *Kobunshi Ronbunshu* **2007**, *64*, 41.

(8) Foulger, S. H.; Jiang, P.; Ying, Y.; Lattam, A. C.; Smith, D. W., Jr.; Ballato, J. *Adv. Mater.* **2001**, *13*, 1898.

(9) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.

(10) de Souza, R. F.; Padilha, J. C.; Goncalves, R. S.; Dupont, J. *Electrochem. Commun.* **2003**, *5*, 728.

(11) Sheldon, R. *Chem. Commun.* **2001**, *23*, 2399.

(12) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.

(13) (a) Sawada, T.; Suzuki, Y.; Toyotama, A.; Iyi, N. *Jpn. J. Appl. Phys.* **2001**, *40*, L1226. (b) Kanai, T.; Sawada, T.; Toyotama, A.; Kitamura, K. *Adv. Funct. Mater.* **2005**, *15*, 25. (c) Kanai, T.; Sawada, T.; Maki, I.; Kitamura, K. *Jpn. J. Appl. Phys.* **2003**, *42*, L655.

(14) (a) Kanai, T.; Sawada, T. *Langmuir* **2009**, *25*, 13315. (b) Kanai, T.; Sawada, T.; Yamanaka, J. *J. Ceram. Soc. Jpn.* **2010**, *118*, 370.

(15) Hiltner, P. A.; Krieger, I. M. *J. Phys. Chem.* **1969**, *73*, 2386.

(16) http://www.chemicalbook.com/ChemicalProductProperty_EN.aspx?CBNumber=CB3182194.

(17) Toyotama, A.; Kanai, T.; Sawada, T.; Yamanaka, J.; Ito, K.; Kitamura, K. *Langmuir* **2005**, *21*, 10268.

(18) (a) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953. (b) Tanaka, T.; Fillmore, D.; Sun, S.-T.; Nishino, I.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980**, *45*, 1636. (c) Ohmine, I.; Tanaka, T. *J. Chem. Phys.* **1982**, *77*, 5725. (d) Katayama, S.; Hirokawa, Y.; Tanaka, T. *Macromolecules* **1984**, *17*, 2641.

(19) Debye, P.; Hückel, E. *Phys. Z.* **1923**, *24*, 185.