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Control of the Optical Band Structure of Liquid Crystal Infiltrated Inverse Opal by a Photoinduced Nematic−Isotropic Phase Transition

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Recently, photonic band gap (PBG) crystals composed of spatially ordered dielectrics with lattice parameters comparable to the wavelength of visible light have received much attention due to their unique properties in controlling the propagation of light.[1−7] Many potential photonic crystal applications require some properties for tuning the band structure through external stimuli. A practical scheme for tuning the band gap using liquid crystals (LCs) has recently been proposed, and indeed electrically and thermally tunable photonic band gap composites have been reported.[8−11] However, the changes in the optical stop band were not so large, and complete switching has yet to be realized. Here, we report on a new type of switchable photonic crystals that exhibits a drastic change in optical properties by taking advantage of the photoinduced phase transition of liquid crystals. The photoswitchable photonic crystals are comprised of SiO_2 inverse opal infiltrated by liquid crystal (LC) and photochromic liquid crystal azo dyes. In this system, the propagation of light is initially inhibited due to light scattering resulting from the randomness of the dielectric constant in the composite inverse opal. When the colloidal crystal film was irradiated by UV light, trans−cis photoisomerization was induced, leading to the nematic-to-isotropic phase transition of the liquid crystal.[12] The appearance of a homogeneous isotropic phase allowed us to observe the stop band in the composite inverse opal. It was possible to reverse this by irradiating the film with visible light, showing that this system is photoreversible. A phototunable composite such as this with good stability and reproducibility may find application in all-light optical devices.

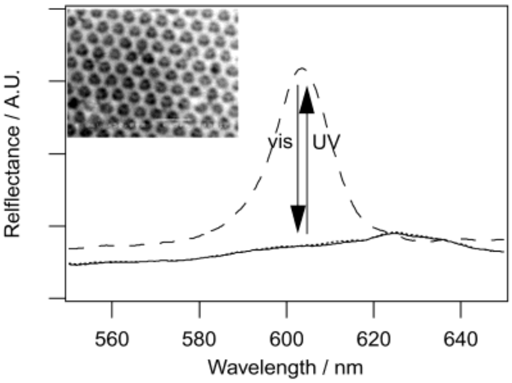

Figure 1. Reflection spectra of AzoLC/5CB infiltrated inverse opal film. The solid line is the spectrum in the original state, the dashed line is that after irradiation by UV light for 60 s, and the dotted line is that following irradiation by visible light for 60 s. An SEM image of SiO_2 inverse opal structure is shown in the inset. The thickness of the film is about 15 μm.

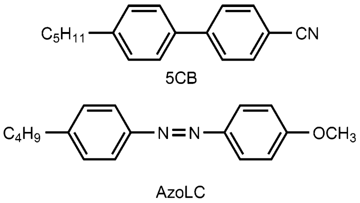

Figure 2. The chemical structures of 5CB and AzoLC.

Photoswitchable photonic crystals were fabricated by infiltrating LCs into inverse opal structure films. The SiO_2 inverse opal films were fabricated on glass substrates using a method developed previously by us.[13] Monodispersed polystyrene spheres with a diameter of 208 nm were used as a template. Figure 1 shows an SEM image of the inverse opal structure. The well-ordered hexagonal structure derived from fcc packed opal can be observed in the top-view image. The voids in the samples were filled with a mixture of 4-pentyl-4′-cyanobiphenyl (5CB, Merck) and 4-butyl-4′-methoxyazobenzene (AzoLC). The fraction of AzoLC was 3% vol. The AzoLC was synthesized via a diazo-coupling reaction between 4-butylaniline and phenol, followed by alkylation with methyl iodide. The chemical structures of 5CB and AzoLC are shown in Figure 2. Note that, when the LCs were infiltrated into the voids, they were heated at 60 °C to put it into the isotropic phase, thereby enabling it to be introduced into the voids.

The optical properties were measured using a multichannel photodetector connected to a Y-type optical fiber. Light from an Hg lamp passed through a band-pass filter was used as an ultraviolet pump. Figure 1 shows the reflection spectra of AzoLC/5CB infiltrated inverse opal films. In the original state, the peak was not clear, although a somewhat ill-defined peaklike feature appears around 630 nm. However, when the composite was irradiated by UV light (light intensity = ca. 1.5 mW/cm^2), a reflection peak at 603 nm increased rapidly and then saturated. After irradiation, an optical stop band appeared as shown in the figure. The trigger for this drastic change was the photoisomerization of the azo derivatives in the films. The excitation of the $\pi-\pi^*$ transition of *trans*-Azo LC at around 360 nm results in a transformation to *cis*-Azo LC with the n$-\pi^*$ transition at about 450 nm. The trans form of azobenzene derivatives has a rodlike shape, which is similar to 5CB, and hence tends to stabilize the phase structure. On the other hand, the photoinduced cis form of azobenzene has a bent shape and hence

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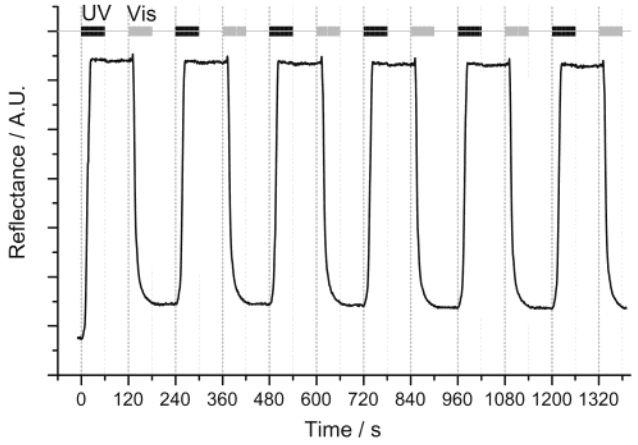

Figure 3. Time-dependent change in the reflectance of 5CB/AzoLC infiltrated inverse opal film at 603 nm by UV and visible light irradiation. The black bars show the periods for the irradiation of UV light (<400 nm), and the gray bars show the periods for irradiation of visible light (436 nm). For other periods, the sample was kept in the dark.

tends to destabilize the phase structure. Therefore, trans-cis photoisomerization of azobenzene in the nematic phase can disorganize the phase structure of nematic LCs.[12] This leads to a nematic−isotropic isothermal phase transition, resulting in a drastic change in the propagation of light in inverse opal.

The observed change could be reversed to the original state by irradiating with visible light. Light from an Hg lamp passed through an interference filter was used as the light source. When the composite was irradiated with visible light (light intensity = 0.75 mW/cm^2) for 60 s, the reflectance decreased rapidly and then almost disappeared. It is surmised that the recovery was induced by cis-to-trans photoisomerization, followed by a phase transition from the isotropic to the nematic phase. Such a switching effect could also be observed in transmission spectra. The change could be induced repeatedly by alternating irradiation with UV and visible light. Figure 3 shows the time-dependent change in the reflectance of inverse opal films at 603 nm. It shows that over six cycles the process is completely reversible, exhibiting good stability and reproducibility during the light irradiation cycle.

It should be noted that, in the inverse opal structure, the LC molecules in the nematic phase in the spheroidal voids are aligned parallel to the void surfaces forming the well-known bipolar structure.[14] Also, the orientation of the polar axes of the bipolar structure of LC in different spheroidal voids is random.[15] As a result, although LC spheres form an ordered structure inside the composite inverse opal, the dielectric constants of LC spheres are completely random. Such a structure does not satisfy the conditions required for Bragg diffraction, and so the light was scattered. Light scattering due to the randomness of the dielectric constant is similar to the phenomena observed for polymer dispersed liquid crystal (PDLC).[15,16] On the other hand, when the liquid crystal was transformed into an isotropic phase by light, the anisotropy in the dielectric constant disappeared. That is, the dielectric constant of the LC in all of the spheroidal voids became the same. This means that the dielectric constant of LC spheres changes from a random state into an ordered one, and hence a reflection peak due to Bragg diffraction appears.[6,7] On the basis of this scenario, we were able to observe a dynamic change in the optical properties in our system. Note that only a small change in the reflectance of the Bragg diffraction peak was observed in SiO$_2$ opal structures infiltrated by the same liquid crystal. This suggests that the changes in the optical properties are strongly dependent on the size and shape of the voids that are filled with liquid crystal.

In a preceding paper, we have shown that the photonic band gap can be controlled by enhancing the dielectric constant near the resonant absorption band.[17] Although the technique provides a way of inducing a shift in the stop band as large as 37 nm, an appropriate photochromic dye should be chosen depending on the position of the stop band. On the other hand, in the present system, the 5CB and azo dyes can be used independently of the wavelength of the stop band. This means that the present system has some versatility. Furthermore, this type of liquid crystal infiltrated inverse opal allows novel switching of the order of dielectrics between a random state and an ordered one. The drastic change in the optical properties of such a composite is ideal for practical applications. The random state is also interesting from the point of view of Anderson localization.[18,19]

In conclusion, we have fabricated photoswitchable photonic crystals based on inverse opal structures by taking advantage of the nematic−isotropic phase transition induced by photochemical isomerization of AzoLC. The on/off switching of reflection by irradiating alternately with UV and visible light was observed and was completely reversible. This dynamic switching of the on/off state gives such a structure the possibility of use in various optical device applications.

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Supporting Information Available: Transmission spectra of 5CB/AzoLC infiltrated inverse opal film (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059.
(2) John, S. *Phys. Rev. Lett.* **1987**, *58*, 2486.
(3) Joannopoulos, J. D.; Meade, R. D.; Winn, J. N. *Photonic Crystals: Molding the Flow of Light*; Princeton University Press: Princeton, NJ, 1995.
(4) Yablonovitch, E.; Gmitter, T. J. *Phys. Rev. Lett.* **1989**, *63*, 1950.
(5) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, *386*, 143.
(6) Tarhan, İ. İ.; Watson, G. H. *Phys. Rev. Lett.* **1996**, *76*, 315.
(7) Park, S. H.; Xia, Y. *Langmuir* **1999**, *15*, 266.
(8) Busch, K.; John, S. *Phys. Rev. Lett.* **1999**, *83*, 967.
(9) Kang, D.; Maclennan, J. E.; Clark, N. A.; Zakhidov, A. A.; Baughman, R. H. *Phys. Rev. Lett.* **2001**, *86*, 4052.
(10) Johri, G. K.; Tiwari, A.; Johri, M.; Yoshino, K. *Jpn. J. Appl. Phys.* **2001**, *40*, 4565.
(11) Mach, P.; Wiltzius, P.; Megens, M.; Weitz, D. A.; Lin, K.-h.; Lubensky, T. C.; Yodh, A. G. *Phys. Rev. E* **2002**, *65*, 31720.
(12) Sung, J. H.; Hirano, S.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Chem. Mater.* **2002**, *14*, 385.
(13) Gu, Z. Z.; Kubo, S.; Fujishima, A.; Sato, O. *Appl. Phys. A* **2002**, *74*, 127.
(14) Luther, B. J.; Springer, G. H.; Higgins, D. A. *Chem. Mater.* **2001**, *13*, 2281.
(15) Kitzerow, H. S. *Liq. Cryst.* **1994**, *16*, 1.
(16) Bouteiller, L.; Barney, P. L. *Liq. Cryst.* **1996**, *21*, 157.
(17) Gu, Z.-Z.; Hayami, S.; Meng, Q.-B.; Iyoda, T.; Fujishima, A.; Sato, O. *J. Am. Chem. Soc.* **2000**, *122*, 10730.
(18) Wiersma, D. S.; Bartolini, P.; Lagendijk, A.; Righini, R. *Nature* **1997**, *390*, 671.
(19) Schuurmans, F. J. P.; Vanmaekelbergh, D.; van de Lagemaat, J.; Lagendijk, A. *Science* **1999**, *284*, 141.

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