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Control of Photonic Band Structure by Molecular Aggregates

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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 garnered great attention for their ability to exercise complete control of the propagation of light.[1−6] For practical applications, it is crucial to obtain some degree of tunability of the photonic band structures through external stimuli, especially light. The fabrication of such tunable photonic band gap (TPBG) crystals is still a challenge. In this report, we show that such TPBG crystals can be realized by taking advantage of the enhanced change in the refractive index that is due to the coherent excitation effect in a molecular aggregate.

The photonic band structures of PBG crystals depend on the spatial periodic structures and the refractive indices of the dielectrics. Changes in the spatial structures induce appreciable changes in the stop-bands (a wavelength region where the propagation of light is forbidden).[7−9] However, the rates at which such changes can be made are usually too low for practical tunable optical devices. Another possible way to tune the stop-band is via the control of the refractive index by use of liquid crystals.[10] However, changes in the refractive index are not necessarily sufficient to give appreciable changes in the photonic band structure. Here, we propose the use of molecular aggregates to control the photonic structure. The molecular aggregate is a collection of molecules, in which the individual molecules are closely coupled and respond in-phase to an external applied field. The electronic coherence in molecular aggregate contributes a giant oscillation.[11] The complex refractive index (n_{cmp}) of a molecular compound, for which the real part is the refractive index (η) and the imaginary part is the extinction coefficient (κ), is expressed by[12]

$$n_{\mathrm{cmp}}^2 = (\eta + i\kappa)^2 = \frac{Ne^2}{\epsilon_0 m}\sum_k \frac{f_k}{\omega_\kappa^2 - \omega^2 + i\gamma_\kappa \omega} \qquad (1)$$

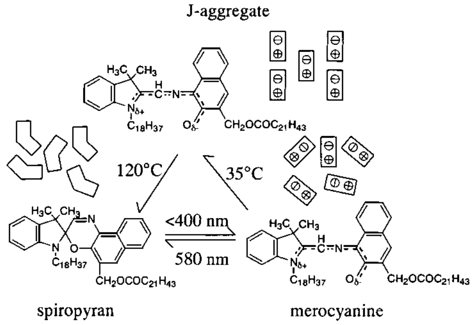

Figure 1. Photochromic reaction of a spiro dye.

where e is the electric charge, m is the electron mass, N is the number of oscillators per unit volume, f_k is the oscillation strength, ω_k is the kth resonant frequency of the dye molecule, and γ_k is the kth damping coefficient due to optical absorption. Apparently, the giant oscillation can induce dramatic changes in the refractive index around the resonant frequency. This suggests that an appropriate choice of photochromic dye aggregate, that is, one in which an oscillation frequency of the aggregated state is close to the photonic band gap, while that of the nonaggregated state is far from the gap, would enable one to induce a large change in the stop-band by illumination.

Phototunable photonic band gap crystals constituted from photochromic dyes and silica spheres were fabricated by evaporating dye into the voids of synthetic opals fabricated by means of the vertical deposition method.[13] We chose a spiro derivative of 1′,3′-dihydro-3′,3′-dimethyl-6-nitro-1′-octadecyl-8- docosanoyloxymethylspiro [2H-1-benzopyran-2,2′-[2H] indole] as our dye molecule (Figure 1). The dye molecule undergoes photoisomerization from the spiropyran form to the merocyanine form upon illumination with UV light, and forms *J*-aggregates in a thermal process. As the resonant absorption of this compound is observed at around 600 nm, silica spheres with diameters of 275 nm (OP1) and 195 nm (OP2) were used to take advantage of the change of refractive index near the resonant oscillation. During the evaporation, the temperature of the opal films was carefully controlled to enable the dye to infiltrate into the voids. UV−visible spectra showed that the dye was in its spiropyran from after infiltration. The thickness of the dyed opal film is about 100 μm.

The (111) faces of the synthetic opals, which had an *fcc* structure after infiltration are shown in Figure 2. The hexagonal ordering of the silica spheres is retained after the infiltration of the dye. OP1 exhibits a normal reflection peak at 635 nm, while that for OP2 appears at 446 nm. These reflection peaks shifted to 725 and 488 nm, respectively, after infiltration of dye. These refractions originate from the stop-bands of the opals at the *L*-point of the reciprocal lattice. The peak wavelength, λ, can be estimated by

$$\lambda = 1.633d\sqrt{(1 - V_{\mathrm{f}})\eta_{\mathrm{void}}^2 + V_{\mathrm{f}}\,\eta_{\mathrm{silica}}^2} \qquad (2)$$

where d is the diameter of the silica spheres, η_{void} and η_{silica} are the refractive indices of silica and of the medium infiltrating the voids, respectively, and V_{f} is the volume fraction of silica spheres in the opal. Infiltration of molecular compounds into the voids

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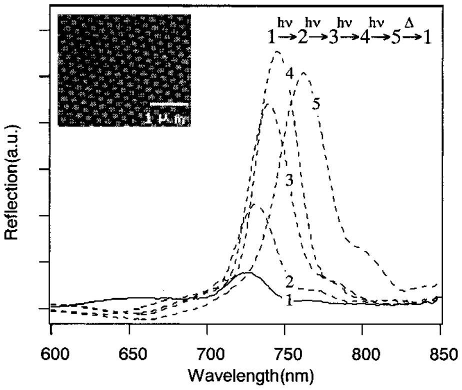

Figure 2. Photoinduced changes in the 0° reflection spectra of the dye-filled OP1. Spectra 1−5 are measured after being irradiated for 0, 1, 3, 10, and 60 min. The notation *hν* indicates the illumination with UV light (<400 nm) and Δ indicates thermal treatment at 120°C. The (111) face of the dyed opal is shown in the inset.

induces a change in η_{void}, and hence in λ. By using the shifts of the reflection peaks, the volume fractions of dye in opals are estimated as being 0.29 and 0.23 for OP1 and OP2, respectively. These values agree with the theoretical value of 0.26 when dye completely fills the voids, indicating that dye was completely infiltrated by this technique.

Illumination effects of the dye were investigated using the Hg−Xe lamp as a light source. A sharp cutoff filter was used to remove light of wavelength greater than 400 nm. The light intensity is 1 mW/cm^2. The temperature of the samples during the irradiation was kept at around 35 °C. The UV−visible spectra at the resonant wavelength of the spiro dye infiltrated into the voids in the opals are consistent with those of conventional films. This suggests that the properties of the dye in the voids are identical with those of the dye in conventional films. The changes in the stop-band after illumination are detected by the reflection spectrum (Figure 2). The reflection peak of the dyed OP1was shifted continuously from 725 to 762 nm during the illumination. This means that the propagation of light in this region can be continuously tuned by UV light. In particular, the light propagation at around 762 nm can be completely switched on and off by illumination. It should be noted that the shift in the stop-band is accompanied by a large enhancement of the peak intensity. Furthermore, it was found that when the temperature was lowered to −150°C, the reflection peak at 762 nm after illumination was further shifted to 767 nm, accompanied with an increase in the intensity of the reflection. For OP2, a continuous blue-shift in reflection with a decrease of intensity was observed. The stop-band of OP2 was shifted to shorter wavelength by 6 nm after illumination. All of the changes induced by the illumination are reversible and can be recovered by raising the temperature to 120 °C.

According to eq 2, this shift of the stop-band may originate from changes in the interparticle distance or reflective index of dye. To test the changes in interparticle distance, which may originate from volume change in the dye during the photochemical reaction, opal with a sphere size of 980 nm was infiltrated with dye. The stop-band of this dyed opal appears at 2441 nm, where there is no change in refractive index of dye after illumination. Experimental results showed that illumination did not induce the shift of the diffraction peak, indicating that any effects due to interparticlar distance can be ruled out. Hence, the illumination-induced shift of the stop-band should be due to the changes in refractive index of the spiro dye by irradiation. The dye is colorless before illumination. Kramers−Kronig (KK) analysis[14] showed that the refractive index of the spiropyran before illumination is almost constant in the visible region (Figure 3). UV light induces photoisomerization from the spiropyran form to the merocyanine form (Figure 1). Additionally, the molecules in the merocyanine form are self-assembled to produce J-type aggregates via a thermal process. In *J*-aggregates, the molecules respond in phase to an external field as long as they are in the same coherence region. Hence, the excitation of a molecule is resonantly transferred to all of the molecules in the coherent region. The transition moment is given by the Frenkel model: $P_k = \sqrt{N}\mu\delta_{kK}$, where μ is the transition moment of one molecule, N is the number of molecules in the coherent region, and K is the wave-vector. The transition moment P_k is macroscopically increased after the formation of the *J*-aggregate, which contributes to an intensive absorption at around 618 nm and cases great changes in refractive indices. As shown in Figure 3, the refractive index increases to 3.0 at 626 nm as a result of illumination. The coherent excitation is responsible for the large change in the stop-band. It is important to note that the refractive index, 3, at 626 nm is larger than that for TiO$_2$. The increase of the refractive index above 600 nm results in a red-shift of the stop-band of OP1. The enhanced changes observed at −150 °C are due to the increase of the coherence size in the *J*-aggregates at low temperature. That is, the number of coherent molecules, *N*, increases with the decrease in scattering at low temperature, leading to an increase of the refractive index. The increase of reflection intensity should be the result of the increase of the mismatch of the refractive indices for silica and the dye. The blue-shift of the band gap of OP2 is a result of the decrease of the refractive indices below 600 nm. The origin of the decrease of the reflective intensity for OP2 should be a result of both the decrease in mismatch of the reflective indices and the attenuation effect due to the extinction coefficient of the dye.

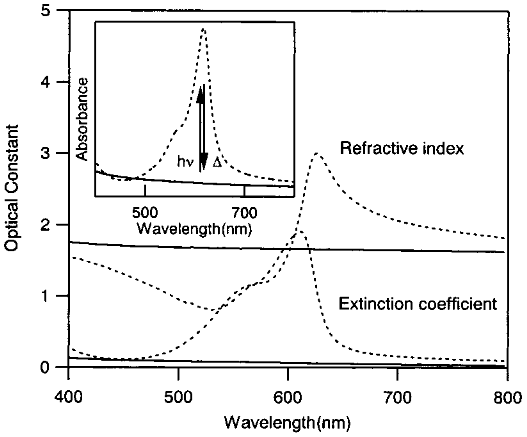

Figure 3. Optical constants of the spiro dye calculated from transmittance spectra by KK analysis. The solid and the dashed lines are curves for the optical constants before and after illumination with UV light, respectively. Insert is the absorption spectra of the dye film. The notations of *hν* and Δ are same as Figure 2.

In summary, we have shown that the change in refractive index induced by the formation of the aggregates is quite large compared with the change induced by an orientation change of liquid crystal molecules or by the photochromic effect at the single-molecule level. Furthermore, the induction of such large changes of refractive indices provides a new approach toward the synthesis of materials with both large and small refractive indices.

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