Photochemically Controlled Cross-Linking in Polymerized Crystalline Colloidal Array Photonic Crystals

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ABSTRACT: We developed photochemically controlled photonic crystals which may be useful in novel recordable and erasable memories and/or display devices. Information is recorded and erased by exciting the photonic crystal with ∼360 nm UV light or ∼480 nm visible light. The information recorded is read out by measuring the photonic crystal diffraction wavelength. The active element of the device is an azobenzene cross-linked hydrogel which contains an embedded crystalline colloidal array. UV excitation forms *cis*-azobenzene cross-links while visible excitation forms *trans*-azobenzene cross-links. The less favorable free energy of mixing of *cis*-azobenzene cross-linked species causes the hydrogel to shrink and blue-shift the photonic crystal diffraction. This is completely the opposite behavior as observed from pendant azobenzene groups we reported previously. We also observe fast nano-, micro-, and millisecond transient dynamics associated with fast heating lattice constant changes, refractive index changes, and thermal relaxations.

Introduction

The recent intense interest in photonic band gap crystals stems from their potential ability to increase light waveguiding efficiency, to increase the efficiency of stimulated emission processes, and to localize light.[1] Numerous groups around the world are developing fabrication methods to produce photonic crystals with band gaps in the visible, infrared, and microwave spectral regions.[2]

The simplest photonic crystal can be fabricated by the close-packing of spheres similar to that which in nature forms opals. The earliest chemical approach fabricated large face-centered-cubic (fcc) photonic band gap crystals through the self-assembly of highly charged, monodisperse colloidal particles into crystalline colloidal arrays (CCAs). The CCAs self-assemble due to long-range electrostatic repulsions between particles.[3,4]

These CCAs are complex fluids which consist of colloidal particles that self-assemble into plastic fcc crystalline arrays which Bragg diffract ultraviolet, visible, or near-infrared light, depending on the colloidal particle array spacings. More recently, robust semisolid photonic crystal (PCCA) materials were fabricated by polymerizing a hydrogel network around the self-assembled CCA array[5] (Figure 1). This new photonic crystal material can be made environmentally responsive such that thermal or chemical environmental alterations result in PCCA volume changes, thereby altering the CCA photonic crystal plane spacings and diffraction wavelengths.[6−10]

We report here the development of a second[11] example of a photochemically actuated PCCA, where photoisomerization of a covalently attached cross-linking chromophore changes the hydrogel free energy of mixing. The resulting photocontrolled PCCA volume change alters the lattice constant and shifts the diffracted wavelength. Thus, we have a material in which we can modulate the diffracted light by exciting the material either with 360 or 480 nm light, far from the diffraction band gap.

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The photonic crystal PCCA described here utilizes photoisomerization of azobenzene cross-links to alter the PCCA diffraction. Photoisomerization of the azobenzene cross-link from its normally trans to its cis form blue-shifts the diffraction. In contrast, our previously demonstrated pendent azobenzene PCCA showed a diffraction red-shift upon azobenzene isomerization to the cis form.[11] Although the photochemistries are identical, as are the mechanisms of diffraction shifting, the detailed solution thermodynamics differ.

Experimental Section

Synthesis of the Azobenzene Cross-Linker. We synthesized azophenyl-*p*-*N*,*N*′-dimaleimide in 53% yield by dissolving 2 g of 4,4′-diaminoazobenzene (Lancaster) in 20 mL of dimethylformamide (DMF, Aldrich) and mixing it into a solution of 5 g of maleic anhydride (Fisher) in 5 mL of DMF.[12] After 2 h, yellow crystals of azophenyl-*p*-*N*,*N*′-dimaleimide were filtered out, dried, and dissolved in 250 mL of acetic anhydride (Fisher) and 12 g of sodium acetate (Aldrich). The liquid was decanted, and its volume reduced under vacuum to 50 mL. 300 g of ice was added to the solution, and after 2 h the crystals were collected and washed with water. Recrystallization of the sample was done twice in (1:1) dioxane−ethanol mixtures. The sample was dissolved in chloroform and its structure confirmed by NMR.

Synthesis of the Photoresponsive PCCA with Photochromic Cross-Links. Monodisperse polystyrene colloidal particles (120 nm diameter) with thousands of sulfonate groups on their surface were synthesized by emulsion polymerization.[13] We dialyzed the colloidal suspension against water for 1 week, after which these particles self-assembled into highly ordered crystalline colloidal arrays (CCA).

Polymerized crystalline colloidal array (PCCA) was prepared by dissolving 50 mg of acrylamide (Sigma) and 3 mg of *N*,*N*′-methylenebis(acrylamide) (Sigma) in 1 g of a 12 wt % colloidal suspension of the polystyrene colloids prepared above. *N*,*N*′-Cystaminebis(acrylamide) (5 mg, Aldrich) and a 10 μL solution of 10% diethoxyacetophenone (DEAP, Aldrich, v/v) in DMSO were then added to the above mixture.

This solution was injected into a cell made of two quartz plates separated by a 80 μm thick spacer and exposed to UV light (Black-Ray model B-100A, UVP Inc.). After 30 min illumination, the cell was opened and the gel was removed and washed with water in order to remove unreacted monomer. The PCCA swells slightly (2 nm diffraction red-shift, diffraction peak at ∼455 nm) as it assumes its equilibrium volume in water.

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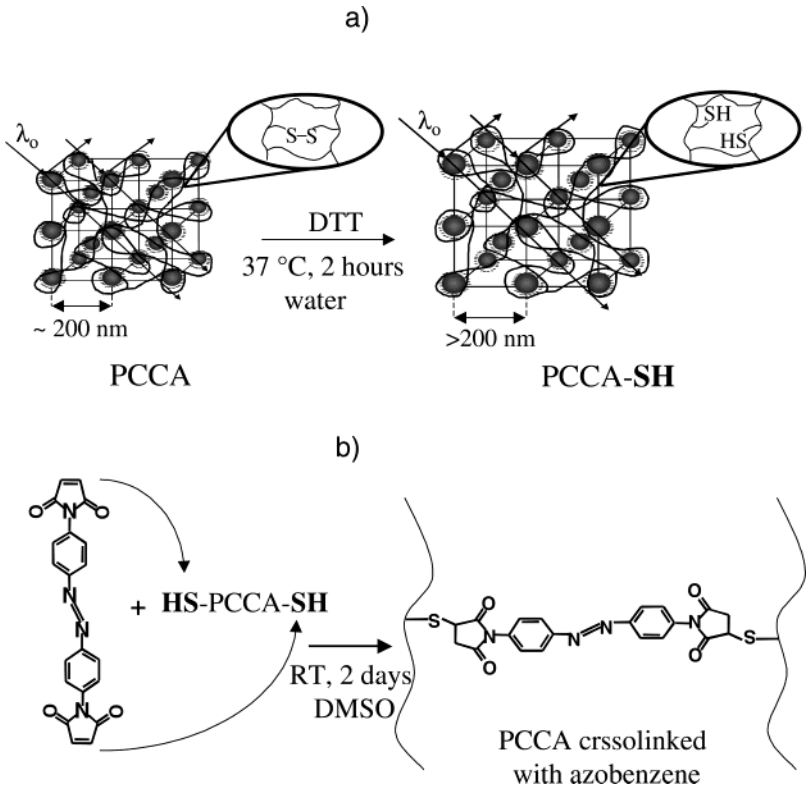

Figure 1. (a) Synthesis of thiol-functionalized PCCA. (b) Synthesizing a photoresponsive PCCA by cross-linking the thiol-functionalized PCCA with azophenyl-*p*-*N*,*N*′-dimaleimide.

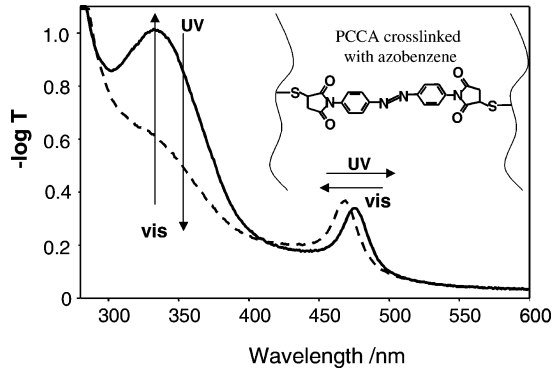

Figure 2. Response of azobenzene cross-linked PCCA to UV and visible light irradiation. UV irradiation by a 3 ns pulse of 355 nm light (1.2 mJ/cm^2) converts most of the trans azobenzene to the cis form. This results in a ~10 nm blue-shift of the ~475 nm diffraction peak. Excitation in the visible converts the *cis*-azobenzene back to the trans form and red-shifts the diffraction peak.

Dithiolthreitol (DTT, 0.3 mM aqueous solution, ACROS Organics) was used to cleave the PCCA disulfide bonds to leave reactive thiol groups on the PCCA (Figure 1a).[14,15] This disulfide cross-link cleavage red-shifts the PCCA diffraction 41 nm (from 455 to 496 nm) due to the resulting decrease in the PCCA elastic constant.[10,16]

The PCCA cleavage medium was slowly exchanged stepwise with pure DMSO, after which the PCCA showed a diffraction peak maximum at 487 nm (Figure 2). The 10 nm diffraction peak blue-shift resulted from the decrease in the free energy of mixing between the PCCA and DMSO compared to water. The PCCA diffraction efficiency decreased due to the smaller refractive index difference between the polystyrene colloids (n = 1.60) and the DMSO medium (n = 1.47) compared to that of water (n = 1.33). Higher diffraction intensities would also be observed with thicker samples than our ~80 μm sample. Below 300 nm, the absorption spectrum shows contributions from diffraction as well as from the polystyrene absorption (Figure 2).

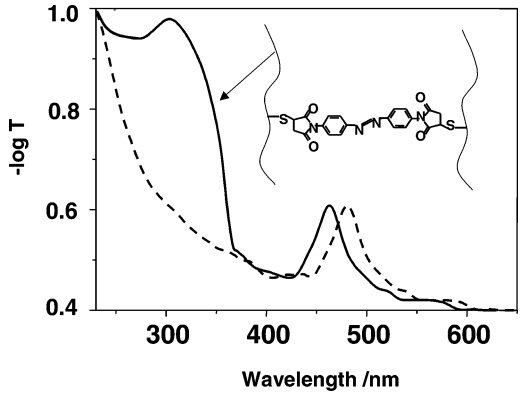

Figure 3. PCCA before (dashed) and after (solid) cross-linking with azophenyl-*p*-*N*,*N*′-dimaleimide.

The cleaved PCCA, which diffracted at 486 nm, was incubated for 2 days at room temperature with a DMSO solution of azophenyl-*p*-*N*,*N*′-dimaleimide (10 mM). Both maleimide groups of azophenyl-*p*-*N*,*N*′-dimaleimide quickly and quantitatively react with the PCCA sulfhydryl groups to form PCCA cross-links.[14,15] The azobenzene PCCA shows a strong *trans*-azobenzene $\pi \rightarrow \pi^*$ absorption band at ~330 nm and diffracts at 464 nm (Figure 2).

Results and Discussion

Photophysics of PCCA Cross-Linked with Azophenyl-*p*-*N*,*N*′-dimaleimide. Figure 3 shows an azobenzene cross-linked PCCA, which has a 475 nm diffraction peak, as well as a strong *trans*-azobenzene $\pi \rightarrow \pi^*$ absorption band at 334 nm. A single 1.2 mJ/cm^2, 3 ns, 365 nm UV laser pulse converts the *trans*-azobenzene to the cis form as evident from the decreased absorbance of the 334 nm absorption band. In response, at long times (seconds to minutes) the diffraction peak blue-shifts 11 nm.

This blue-shift is exactly opposite to the red-shift we previously demonstrated[11] in azobenzene PCCA where

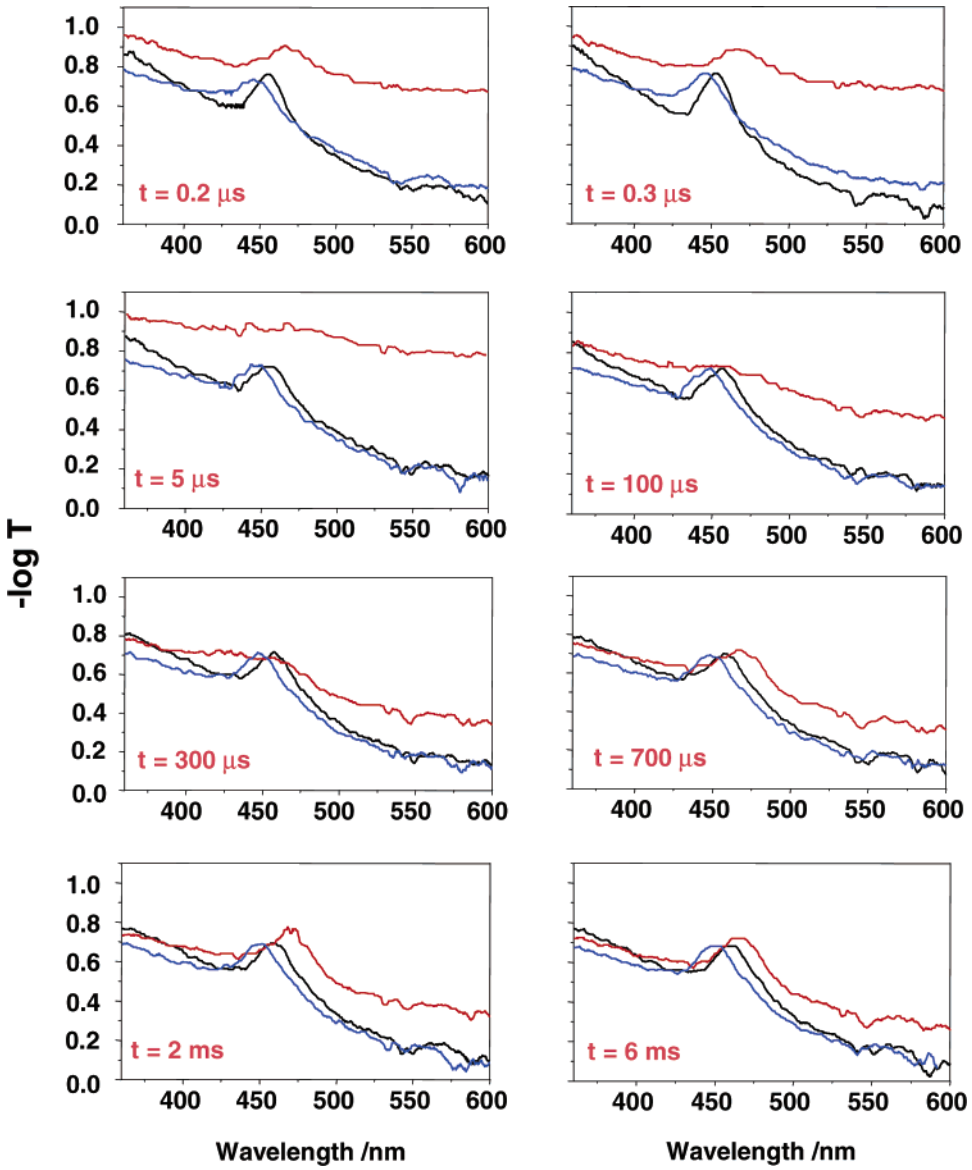

Figure 4. Azobenzene cross-linked PCCA prior to UV excitation (black), at the indicated time after UV excitation by a single 3 ns 355 nm pulse (red), and 1 min (blue) after UV excitation.

the azobenzenes were attached as pendant groups; in that case the formation of *cis*-azobenzene caused the swelling of the hydrogel and red-shifted the PCCA diffraction. This observed blue-shift is completely reversible; visible excitation converts the azobenzene back to the trans form, and the diffraction red-shifts back to the original diffraction wavelength.

Diffraction Kinetics. Figure 4 shows the kinetics of the diffraction changes induced by UV excitation in the nanosecond and microsecond time regimes. The response time of the PCCA depends on the actinic power, the photophysics rate, and the collective diffusion constant of the hydrogel. We examined the kinetics of the diffraction changes by monitoring changes in the transmission spectrum of the sample after applying a single 3 ns, 355 nm YAG pulse (1.2 mJ/cm^2). A 120 ns pulsed Xe flashlamp (IBH model 5000XeF) and Ocean Optics USB2000 miniature fiber-optic spectrometer recorded the transmission spectra at variable time delays between 200 ns and 6 ms after the UV pulse. Figure 4 also shows spectra recorded before (black) and 1 min after the UV pulse (blue). Figure 5 graphically shows the time dependence of the diffraction maximum wavelength in the microsecond and second time scales.

We observe a ~15 nm initial red-shift at 200 ns due to heating of the sample by the UV laser pulse.[11] This shift is ~3-fold greater than that observed for our previous pendant[11] azobenzene PCCA. Presumably, this larger red-shift results from the larger temperature jump induced by the ~2-fold increased azobenzene concentration present in the azobenzene cross-linked PCCA. We calculate that our UV pulse beam induces a ~40 °C temperature jump in the sample which expands the PCCA volume, which increases the d_{111} spacing to red-shift the diffraction.

The PCCA transiently disorders in the 100 μs time scale, which causes the diffraction band to broaden and to disappear. The system then thermally reequilibrates in the ~200 μs to millisecond time scale to restore the original diffraction peak wavelength. At longer times the pendent azobenzene PCCA hydrogel swelled in response to the more favorable free energy of mixing of the larger dipole moment *cis*-azobenzene with the DMSO. This red-shifted the diffraction. Similar photochemistry was used by Wilcox et al.[17,18] in their develop-

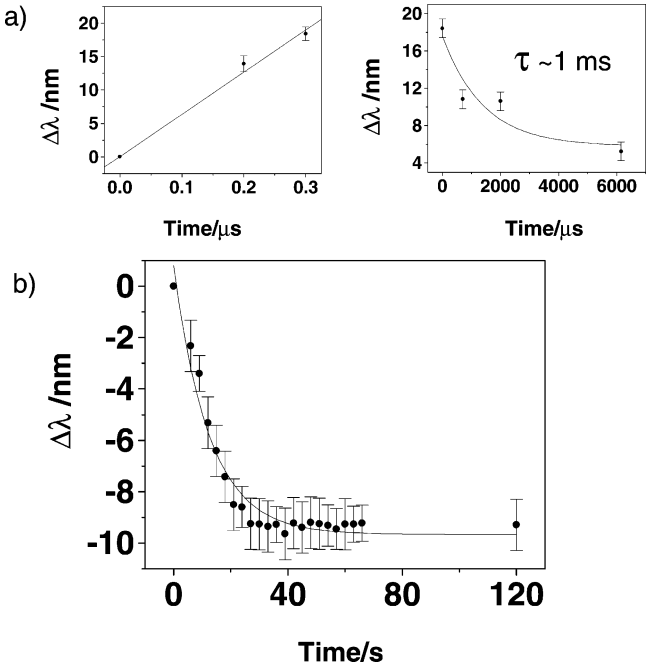

Figure 5. Time dependence of diffraction maximum wavelength in the millisecond (a) and second time scales (b).

ment of a "precipiton" solubility switch activated by isomerization.

In contrast, the azobenzene cross-linked PCCA diffraction blue-shifts by ~11 nm with a characteristic time of ~12 s, showing just the opposite behavior to the pendant azobenzene PCCA derivatives. The origin of the blue-shift is most likely the formation of less soluble hydrogel aggregates by the *cis*-azobenzene cross-linked species. Evidence for this phenomenon comes from the study of Kang et al.,[19] who examined the temperature dependence of the volume phase transition of poly(*N*-isopropylacrylamide) hydrogels with azobenzene cross-links. They found a lower transition temperature for the *cis*-azobenzene compared to the *trans*-azobenzene derivative. They gave an entropic argument to explain the phenomena.

We choose to utilize a more molecular explanation which notes that the decreased transition temperature requires a more hydrophobic and less soluble hydrogel in the presence of the *cis*-azobenzene cross-link. This suggests that the blue-shift results from a less favorable free energy of mixing of the cis-derivative with the medium. This is occurring despite an increased dipole moment, that in the pendant PCCA results in a red shift. It appears that the change in structure of the cis cross-linked hydrogel species causes a more than compensating solubility decrease.

The azobenzene cross-link tethers two segments of hydrogel chains at the cross-link sites, that at the length of the trans derivative possess separate sheaths of solvent. In contrast in the cis derivative, the distance between hydrogel chains is too small for separate sheaths of solvent. As a result, the hydrogel locally collapses and the volume on average contracts. The resulting cross-linked segment appears less soluble, which causes the hydrogel to shrink and blue-shift. The smaller *cis*-azobenzene cross-link creates an excluded volume for solvent molecules in which the hydrogel chains form less soluble segments.

Conclusion

We have developed a new optical memory material which utilizes a PCCA containing azobenzene cross-links. UV excitation converts the ground-state *trans*-azobenzene cross-links to *cis*-azobenzene cross-links. The cis cross-links are indefinitely stable in the dark. Blue light converts the cis cross-links back to the trans. UV excitation results in short and long time diffraction changes. In the fast nanosecond time regime, heating increases the PCCA volume and red-shifts the diffraction. This volume change relaxes in the microsecond time domain. At longer times the volume of this PCCA hydrogel is controlled by the balance between the free energy of mixing of the polymer hydrogel with DMSO and the elastic restoring force of the hydrogel cross-links. We observe a decreased free energy of mixing of the PCCA with the DMSO solvent for the *cis*-azobenzene derivative.

We can photochemically control the diffraction of this photonic crystal; a UV light pulse can write information, and a visible blue pulse can erase it. The information is read out from the diffraction, which can occur at any desired wavelength. To our knowledge, this is only the second[11] example of the photochemical control of a photonic crystal.

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