Photonic Crystal Devices

Marta Kamenjicki[1], R. Kesavamoorthy[2] and Sanford A. Asher[1]
[1]Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA
[2]Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

Abstract. We developed photochemically controlled photonic crystals which may be useful in novel recordable and erasable memories and/or display devices. These materials can operate in the UV, visible or near IR spectral regions. Information is recorded and erased by exciting the photonic crystal with ~ 360 nm UV light or ~ 480 nm visible light. The recorded information is read out by measuring the photonic crystal diffraction wavelength. The active element of the device is an azobenzene functionalized hydrogel which contains an embedded crystalline colloidal array. UV excitation forms cis-azobenzene while visible excitation forms trans-azobenzene. Larger dipole moment of the cis-form results in decrease of the free energy of mixing which causes the hydrogel to swell and to red-shift the photonic crystal diffraction with a 36 s time constant. We also observed fast ms and sub-ms transient dynamics associated with convection due to heating of the medium by UV excitation. Convective motion of the medium stretches the PCCA for about 6 μs within which the convection decays and the elastic restoring force of the PCCA brings back the stretched PCCA to its equilibrium state with 33 μs time constant.

1. Introduction

The recent intense interest in photonic bandgap crystals stems from their potential ability to increase light wave-guiding 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 bandgaps in the visible, infrared and microwave spectral regions [2]. The earliest chemical approach fabricated large face centered cubic (fcc) photonic bandgap crystals through the self-assembly of highly charged, monodisperse colloidal particles into crystalline colloidal arrays (CCAs). These CCAs are complex fluids which 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 semi-solid photonic crystal materials were fabricated by polymerizing a hydrogel network around the self-assembled CCA array (PCCA) [3] (Fig. 1). This new photonic 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 [4].

We report here the development of a photochemically actuated PCCA (120 nm diameter polystyrene CCA), where photoisomerization of a covalently attached 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 modulate the diffracted light by the absorption of the independent light outside the diffraction bandgap.

2. Experimental Description

The highly sulfonated, 120 nm diameter monodisperse colloidal particles were prepared by emulsion polymerization [5]. N,N'-cystaminebisacrylamide (5 mg; Aldrich) dissolved in 20 ml DMSO was added to 4 mg of a solution of 10 % diethoxyacetophenone (DEAP, Aldrich, v/v) in DMSO. The PCCA were prepared by adding this mixture to a solution containing 50 mg acrylamide (Sigma), 3 mg

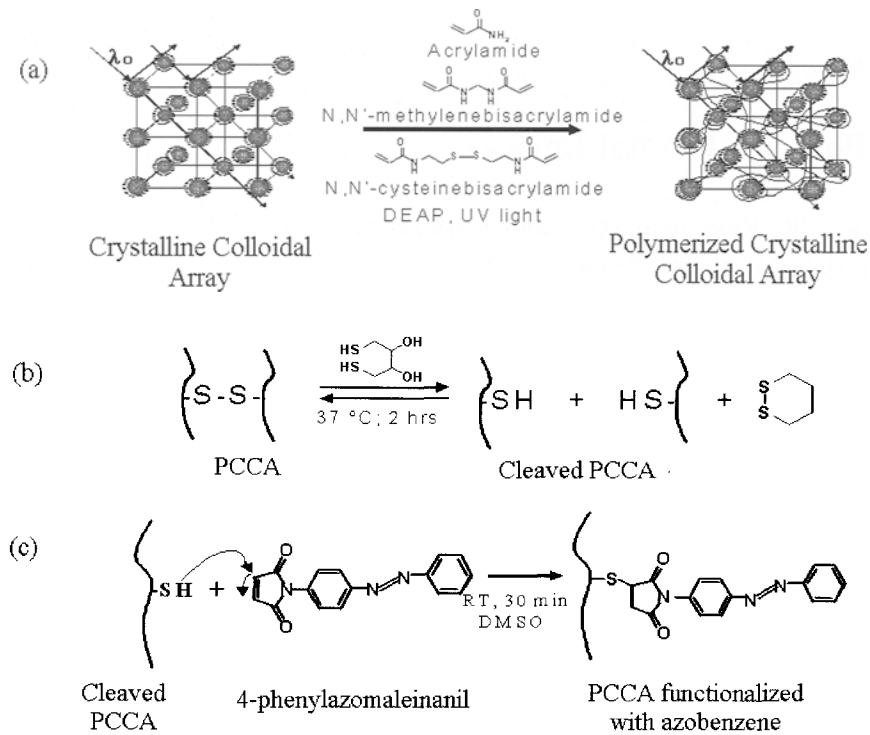

Fig. 1. (a) Synthesis of the PCCA containing disulfide bonds (b) Cleaving disulfide bonds with DTT (c) Maleimide-thiol attachment of azobenzene to PCCA.

N,N'-methylenebisacrylamide (Sigma), and 1 g of a 10 wt.% dispersion of diffracting polystyrene CCA (Fig. 1a). This solution was injected into a cell made of two quartz plates separated by 80 μm thick spacer and exposed to UV light (Black-Ray model B-100A, UVP Inc.) for 30 min. The PCCA remained attached to one of the quartz plates. Dithiolthreitol (DTT, ACROS Organics) was used to cleave the PCCA disulfide bonds (Fig. 1b), which leaves reactive thiol groups attached to the PCCA [6]. The PCCA was incubated under stirring for ~ 2 hours with a solution of 4-phenylazomaleinanil (Polysciences, Inc) (Fig. 1c) in dimethylsulphoxide (DMSO) (7 mM). The PCCA containing covalently attached azobenzene shows diffraction from the fcc (111) planes at ~540 nm and the trans azobenzene absorption band at 322 nm. We can vary the amount of attached azobenzene by controlling the sulfhydryl group concentration within the PCCA.

3. Results and Discussion

Figure 2. shows the absorption spectrum of a PCCA containing covalently attached azobenzene. Excitation with 365 nm UV light (~ 13 mW/cm^2) results in a decrease in the 322 nm ($\pi \rightarrow \pi^*$) trans absorption and an increase in the 430 nm ($n \rightarrow \pi^*$) cis absorption, due to the photoconversion of the trans to cis form (the absorption shifts to 322 nm upon attachment to the PCCA). The PCCA was oriented such that the beam was incident normal to the fcc (111) planes, which at this normal incidence diffracts ~ 530 nm light. The conversion of trans-azobenzene to the cis-form causes the (111) plane diffraction to red-shift from ~ 530 nm to ~ 580 nm. Excitation with visible light (~ 3 mW/cm^2) shifts the diffraction back to ~ 530 nm. This photochemically driven diffraction change is reversible. Irradiation of a PCCA for 5 min with ~ 10 mW/cm^2 UV light causes a ~ 0.2 absorbance decrease at ~ 322 nm and a ~5 nm diffraction red-shift, which is completely reversed with a 1 min illumination with ~ 50 mW/cm^2 visible light. The PCCA absorption and diffraction can be cycled back and forth indefinitely [7].

We examined the kinetics of the changes in the diffraction by monitoring changes in the transmission

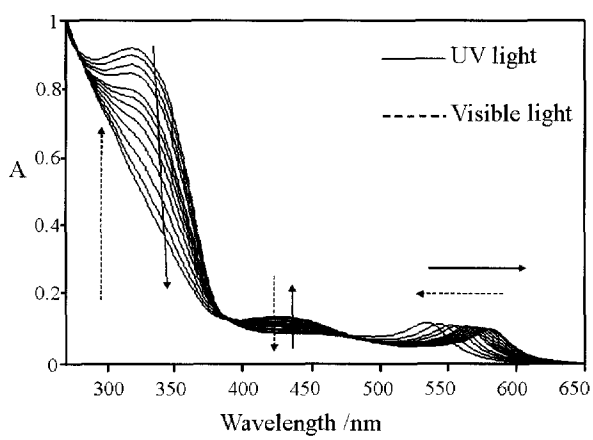

Fig. 2. 80 mm thick PCCA functionalized with 4-phenylazomaleinanil (3 mM) shows a 50 nm diffraction red-shift upon UV excitation. Solid arrows show spectral changes due to the UV irradiation, while the dashed arrows show changes due to visible light illumination. The 530-600 nm peak derives from diffraction by the PCCA fcc (111) planes. The (111) plane spacing, $d_{111} = \lambda_o/2n$ for light at normal incidence.

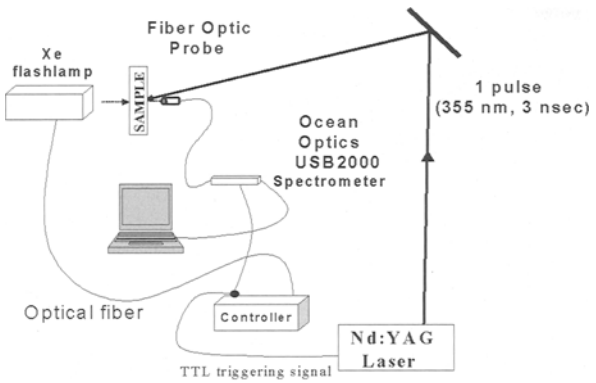

Fig. 3. Transient absorption spectrophotometer used to measure PCCA spectral kinetic responses to 355 nm light.

spectrum of the sample after applying one 355 nm YAG pulse (1.2 mJ/cm^2, 3 ns duration). We used a 120 ns pulsed Xe flashlamp (IBH Model 5000XeF) and Ocean Optics USB2000 Miniature Fiber Optic Spectrometer (Fig. 3), and recorded spectra after time delays of 0.3 μs to 6 ms, and 3 s to 2 min subsequent to UV pulses. A diffraction red-shift of ~ 5 nm occured within 300 ns. The diffraction peak remained sharp and symmetric. At 1.3 μs we saw more complex dynamics where the background increased and the diffraction broadened. The diffraction continued to red-shift until ~ 12 μs but was very broad and difficult to locate the diffraction peak. By 20 μs the diffraction began to narrow and the diffraction band started blue-shifting. At 302 μs only a small diffraction red-shift remained; the diffraction spectrum was close to that prior to the UV pulse. Much larger diffraction changes (~ 10 nm) occured at much longer times. Temporal dependence of the diffraction peak wavelength is shown in Fig. 4 for all the time regimes.

Excitation of trans-azobenzene attached to 2 cm × 2 cm × 80 μm PCCA in dimethyl sulphoxide (DMSO) solvent with 3 ns 355 nm UV laser pulse of 2 mm diameter results in the formation of cis-azobenzene. Thermalisation of the excited cis heats up the surrounding DMSO to 20 °C above the ambient. Heat transport from this hot region to the colder outer region results in the convective motion of DMSO which stretches the PCCA by carrying the colloidal particles along the convective flow lines. Due to this stretching, the diffraction wavelength of the PCCA increases with time for about 12 μs. In this time scale, the convection decays and the stretched PCCA relaxes back exponentially to its equilibrium state with 33 μs time constant due to its elastic restoring force. We modeled the stretching force due to the convection to be proportional to the pressure gradient in the PCCA which reduces linearly with stretching. The pressure gradient is derived from the pressure jump at the UV laser spot. The pressure jump is the result of the fractional volume increase (0.0186) due to the heating by thermalization of the cis and the bulk modulus of the DMSO. Opposing this expansion force is the elastic restoring force of the PCCA which tries to bring back the PCCA to its equilibrium state. When thermal equilibrium is reached, the convection decays, the stretching force becomes zero and the elastic restoring force causes the PCCA to relax exponentially with 33 μs time constant. Our model fits the experiment well as seen in Fig. 4 for the PCCA osmotic pressure modulus of 9225 dynes/cm^2. Our modulus calculation predicts the effective crosslinker fraction as 0.17. Even lower crosslinker fraction has been reported for similar PCCA [8].

The fact that the 355 nm absorption remains bleached, demonstrates that the slow process of 36 s time constant red-shift does not involve azobenzene trans to cis ground state photochemistry. The cis has dipole moment (3.5 D) whereas the trans has not. The cis dipole moment produces an electric field around it. The DMSO dipoles (4.3 D) are attracted and oriented around it. We could place 6 DMSO dipoles in the first solvation shell around each cis dipole, 5 at about 0.47 nm and 1 at 0.37 nm separation distance. This results in −1523 erg dipolar attraction energy (ΔU) in the heated PCCA volume containing 8.67 × 10^{14} cis dipoles as compared to that for trans. Orientation of DMSO around cis causes the entropy energy (TΔS) to decrease by −1509 erg whereas no DMSO is ordered around a trans. Thus, the free energy of mixing of the polymer network in DMSO (ΔU + PΔV − TΔS) decreases by −14 erg, where PΔV is found to be negligible. This decrease of free energy of mixing causes

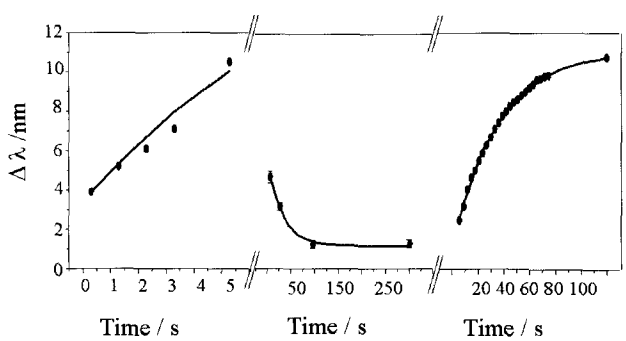

Fig. 4. Temporal dependence of diffraction peak wavelength after excitation by a 3 ns 355 nm laser pulse. Solid lines are the theoretical fit.

the hydrogel to expand into a new equilibrium state. This dynamics results in the exponential increase of the PCCA diffraction wavelength with 36 s time constant decided by the frictional diffusion of the polyacrylamide 3D network in DMSO. The fit to the experimental diffraction red-shift in 100 s time scale was also very good (Fig. 4) with the same osmotic pressure modulus used for the 33 μs time scale relaxation. The osmotic pressures due to free energy of mixing, elastic restoring force and Donnan potential [8] in a PCCA add upto zero at equilibrium. We calculated the Flory-Huggins χ parameter for the free energy of mixing as 0.5047 and 0.5018 in the trans and the cis PCCA, respectively. A decrease in χ implies an increase in hydrophilicity due to increased mixing of the polymer network in DMSO caused by the cis dipole moment. This decrease in χ results in −13.4 erg decrease in the free energy of mixing which matches well with that calculated from ($\Delta U + P\Delta V - T\Delta S$).

4. Conclusion

Diffraction switching in our photoresponsive PCCA results from both azobenzene photoisomerization and laser heating. In the fast μs time regime, heating causes the DMSO convection, stretches the PCCA and red-shifts the diffraction for ~ 12 μs. This volume change relaxes with 33 μs time constant when the convection decays. At longer times, the PCCA hydrogel volume is controlled by the balance between the free energy of mixing of the polymer hydrogel in DMSO and the elastic restoring force of the hydrogel crosslinks. The cis-isomer dipole moment results in an increased solubility in DMSO, causing an increase in the free energy of mixing. Thus, the PCCA swells and a diffraction red-shift is observed. To our knowledge, this is the first example of the photochemical control of a photonic crystal.

5. References

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