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Nanogel Nanosecond Photonic Crystal Optical Switching

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Abstract: We developed a robust nanosecond photonic crystal switching material by using poly(*N*-isopropylacrylamide) (PNIPAM) nanogel colloidal particles that self-assemble into crystalline colloidal arrays (CCAs). The CCA was polymerized into a loose-knit hydrogel which permits the individual embedded nanogel PNIPAM particles to coherently and synchronously undergo their thermally induced volume phase transitions. A laser *T*-jump from 30 to 35 °C actuates the nanogel particle shrinkage; the resulting increased diffraction decreases light transmission within 900 ns. Additional transmission decreases occur with characteristic times of 19 and 130 ns. Individual NIPAM sphere volume switching occurs in the ~100 ns time regime. These nanogel nanosecond phenomena may be useful in the design of fast photonic crystal switches and optical limiting materials. Smaller nanogels will show even faster volume phase transitions.

Introduction

There is intense interest in the use of photonic crystals to control propagation of electromagnetic radiation.[1] The simplest photonic crystals possess one-dimensional periodic modulations in their optical dielectric constant.[1] This creates a diffracting structure that prevents transmission of light meeting the Bragg condition. These devices can be used as optical filters. High rejection efficiencies occur for thin films of these materials (~100 μm) for low dielectric constant modulations of <10%. These types of one-dimensional photonic crystals[2-5] can be prepared by utilizing crystalline colloidal array (CCA) self-assembly to form fcc arrays of colloidal particles.[2-8] Alternatively, polymer microphase separation self-assembly can be used to create layered periodic structures.[9] One-dimensional photonic crystals can also be created layer by layer through the chemical vapor deposition techniques used to form dielectric mirrors and filters.[10]

If the modulation amplitude of the dielectric constant could be quickly altered, these materials could be utilized for optical switching. If the incident light beam illumination increased the dielectric constant modulation, this would result in negative feedback for transmission, and these materials could function as optical limiters for sensor and eye protection. The challenge is to develop optically nonlinear photonic crystal materials, which can efficiently control diffraction on fast time scales. This is a severe challenge since most materials have small optical nonlinearities. In the work here we demonstrate that we can utilize nanogels to switch photonic crystal light transmission on the nanosecond time scale.

Experimental Section

These nanogels are composed of the stimuli-responsive polymer poly(*N*-isopropylacrylamide (PNIPAM). PNIPAM has long been known[11] to undergo a volume phase transition when heated above a lower critical solution temperature (LCST) of ~32 °C. Below this critical temperature, the polymer hydrogel is highly swollen in water. Increasing the temperature above the LCST causes the polymer hydrogel to collapse and squeeze out water. The time scale for this volume phase transition is minutes and seconds for macroscopic hydrogels,[12-21] due to the slow rate that water enters or leaves the hydrogel in response to the hydrogel volume phase transition osmotic pressure driving forces. The kinetic response is expected to be diffusional, and the rate of volume change should scale as l^{-2}, where l is the relevant length scale.[12-21] Thus, small hydrogel particles should be able to undergo fast, microsecond and nanosecond phase transitions. Indeed, recent turbidity studies by Lyon's group of individual ~200 nm PNIPAM colloids show evidence for small nanosecond to microsecond volume phase transitions upon laser *T*-jumps.[22]

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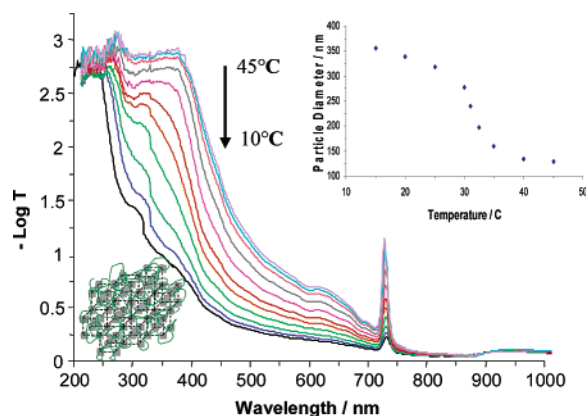(21) Tokita, M.; Miyamoto, K.; Komai, T. *J. Chem. Phys.* **2000**, *113*, 1647−50.

Figure 1. Temperature-dependent extinction spectra of the PNIPAM PCCA with the diffraction peak maximum at 720 nm. The upper right inset shows the PNIPAM colloidal particle's diameter temperature dependence (QELS), and the lower left inset is a cartoon showing the PCCA structure.

Our PNIPAM nanogel particles were synthesized using methods we previously demonstrated would give rise to robust self-assembling CCA crystals.[23] We embedded these NIPAM CCAs in a loose acrylamide hydrogel. We added 1.4 mmol of acrylamide (AMD; Fluka), 32 μmol of *N,N*-methylenebisacrylamide (bis-AMD; Fluka), and 0.24 μmol of 2,2-diethoxyacetophenone (DEAP; Acros Organics) to a 2 mL CCA of diffracting PNIPAM nanogel particles ($\sim$10 wt %) at 40 °C. The resulting solution was injected into a 1 mm path length cuvette (Vitrocom and NSG Pecision Cells, Inc.). These samples were then allowed to cool to room temperature with occasional agitation. The diffracting samples were then slowly photopolymerized over 24 h at room temperature by using attenuated UV light from a Blak Ray (365 nm) mercury lamp. The polymerized CCAs (PCCAs) were washed with pure water.

Results and Discussion

At $\sim$10 °C these PNIPAM particles are highly swollen, showing a diameter of 350 nm by QELS (Figure 1, inset). As the temperature increases the particles shrink and expel water; the diameter decreases to $\sim$125 nm at 40 °C. The swollen particles scatter little light because their dielectric constant differs little from that of water. However, as the particles shrink, their scattering cross section, Q, increases as $Q \approx KD^{-2}$, where D is the particle diameter.[23]

The PNIPAM particle diameter continues to depend on temperature even after self-assembly into a CCA photonic crystal.[23] At low temperature the swollen particles contribute a negligibly small dielectric constant modulation, which gives rise to little diffraction. A temperature increase to $\sim$35 °C causes the particles to collapse; the resulting increased dielectric constant modulation results in efficient diffraction.[23]

Unfortunately, this diffraction change only occurs over long time scales (seconds to minutes). Our initial attempts to induce fast optical switching from laser *T*-jumps resulted mainly in changes in the diffuse scattering as individual spheres changed size in response to the *T*-jumps, but no increased diffraction from the array was observed. The nanogel volume changes presumably disordered the fragile CCA.

In the work here we polymerized a CCA of PNIPAM nanogel particles[23] into a macroscopic acrylamide/bisacrylamide hydro-

gel[24,25] (PCCA; Figure 1). The polymerization occurred under conditions that the individual PNIPAM nanogel particles maintained their temperature-induced individual volume phase transitions. The acrylamide/bisacrylamide hydrogel appears to constrain the centers of mass of the nanogel particles within the fcc lattice and prevents disorder upon the *T*-jump which may cause flow. This PCCA shows diffraction switching in the nanosecond time domain.

For the *T*-jump measurements the mainly aqueous PCCA samples were deuterium exchanged by extensive washing with D_2O while the PNIPAM particles were temperature cycled. This decreased the water absorption at the 1.9 μm pump wavelength. Figure 1 shows the steady-state transmission temperature dependence of this PNIPAM PCCA photonic crystal. The diffraction at $\sim$720 nm derives from the fcc 111 planes of the PCCA photonic crystal, which are mainly oriented perpendicular to the incident beam.

The broadly rising shorter wavelength diffraction results from defects in this somewhat polycrystalline sample; a perfectly ordered and aligned fcc single crystal would show, for normally incident light, diffraction only from the 111 plane at λ_{111}, and no diffraction at shorter wavelengths, until a wavelength of $\lambda_{111}/2 = 360$ nm, in our case.[26] As we demonstrated previously[26,27] lattice misalignments can result in complex diffraction patterns at wavelengths $> \lambda_{111}/2$.

Figure 1 demonstrates that at 10 °C the PNIPAM PCCA diffraction is weak, since the particles are mostly water, which results in only a small dielectric constant modulation.[23] As the temperature increases the particles collapse, expelling water, which increases the dielectric constant modulation, which dramatically increases the diffraction efficiency. For example, at 45 °C less than 10% of the light at 720 nm and less than 0.1% of the light at 400 nm transmits.

We measured the rate of the optical switching by utilizing a transient *T*-jump absorption spectrometer, which excites the sample with a 1.9 μm 3 ns pump pulse, which was absorbed by residual H_2O to heat the sample. A delayed Xe flashlamp white light $\sim$120 ns pulse probed the transmission, which was monitored with a fiber optic diode spectrometer.

Figure 2 displays the temporal evolution of the extinction ($-\log T$) of a second sample (where $\lambda_{111} = 605$ nm) originally at 30 °C after a 5 °C *T*-jump pulse. The extinction increases with time at all wavelengths, with the largest increase at the 111 plane diffraction peak and at the shortest wavelengths. A much smaller extinction increase occurs at wavelengths longer than λ_{111}.

As shown by Figure 3, these extinction changes show at least three different kinetic components. The shortest time $\sim$900 ns kinetics accounts for $\sim$25% of the transmission change, while the longer time $\sim$20 μs kinetics accounts for another $\sim$25%. The longest $\sim$140 μs kinetics accounts for the remaining 50% extinction increase. We find no evidence of longer time kinetics.

These diffraction changes in the PCCA of nanogel particles derive from the coupled volume phase transitions of the PNIPAM particles as shown by the *T*-jump (from 30 to 33.4

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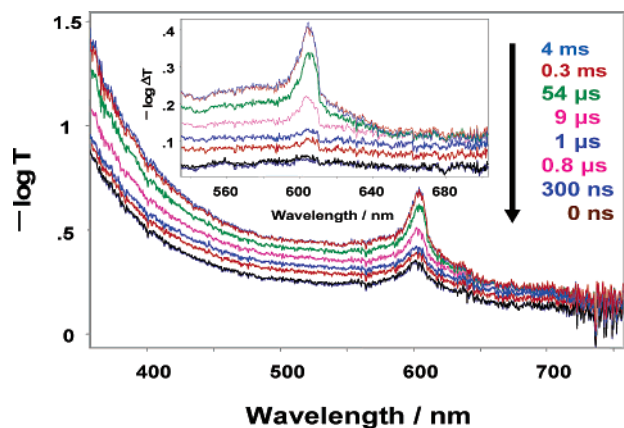
Figure 2. Extinction time evolution for a PNIPAM PCCA sample after a *T*-jump from *T* = 30 °C to *T* = 35 °C. The fcc 111 diffraction peak maximum occurs at 605 nm. Spectra were measured at the times listed, after the *T*-jump. The inset displays difference spectra which highlight the *T*-jump spectral changes.
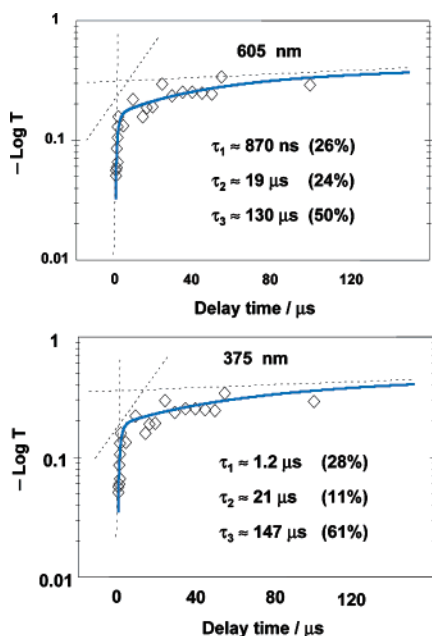

Figure 3. Kinetics of the extinction at 605 nm (upper graph) and 375 nm (lower graph) after a ∼5 °C *T*-jump. Similar triexponential kinetics are observed.

°C) kinetics of the turbidity of a random dispersion of these NIPAM nanogel particiles. The *T*-jump initiates an increased scattering cross section of the particles, which causes a turbidity increase, which causes the transmission to decrease with a single-exponential time constant of ∼100 ns (Figure 4).

At 600 nm we see scattering cross section changes, which occur much faster than Lyon et al.[22] observed for their PNIPAM particle shrinkage. In addition, we do not see any time lag in response after the *T*-jump. This difference in behavior may result from differences in the chemical composition of Lyon et al.'s versus our NIPAM nanogel particles. The rate of a volume phase transition depends strongly on the osmotic pressure induced by the *T*-jump and the cross-link density, which depends on the polymer composition and architecture.[28]

We see even larger cross section changes and a more complex behavior at shorter wavelength (Figure 4). For example, at 370 nm we see three kinetic components at 100 ns (31% transmission
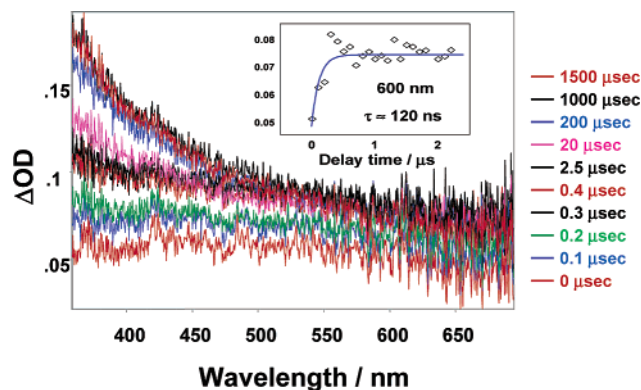

Figure 4. Kinetics of *T*-jump (from 30 to 33.4 °C) turbidity changes. Times listed are after the *T*-jump. The inset shows single-exponential kinetics at 600 nm. More complex kinetics occurs at shorter wavelengths.

decrease), 20 μs (45% transmission decrease), and 350 μs (23% transmission decrease). The scattering cross section decreases result from changes in NIPAM sphere diameter and volume fraction, within a medium with an almost fixed optical dielectric constant. According to Mie theory, there should be only a modest wavelength dependence for light scattered by the cold, large spheres ($\lambda < d$).[29] The hot, smaller spheres scatter in the Rayleigh−Gans regime, where shorter wavelengths will scatter more efficiently than longer wavelengths.[29] Thus, as the temperature increases we expect an increased shorter wavelength scattering.

The increased kinetic complexities observed for the random PNIPAM particles at the shorter wavelengths presumably result from inhomogeneities in the sphere shrinkage dynamics; shorter wavelengths have larger scattering cross sections for smaller refractive index inhomogeneities.[28]

This multiexponential shrinking may result from differences in composition of the interior versus the periphery of these nanogel particles.[22,30−37] The periphery of these particles may have fewer cross-links and be more hydrophilic than the core. The osmotic pressure that actuates the shrinkage would be spatially inhomogeneous, which could lead to complex kinetics.

Conclusions

We developed a robust submicrosecond photonic crystal switching material using nanogel PNIPAM colloidal particles that self-assemble into crystalline colloidal arrays. The array was polymerized into a hydrogel, which permits the individual hydrogel-embedded PNIPAM particles to undergo thermally-induced volume phase transitions. A laser *T*-jump from 30 to 35 °C actuates the nanogel particle shrinkage; the resulting increased diffraction decreases the light transmission within 900 ns. Individual NIPAM sphere switching occurs in the ∼100 ns time regime. These nanogel nanosecond phenomena may be

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useful in the design of fast photonic crystal switches and optical limiting materials. Smaller nanogels will show even faster volume phase transitions. This may be the first example of the induction of a coherent, synchronous material optical response induced by a *T*-jump.

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