Thermally Switchable Periodicities and Diffraction from Mesoscopically Ordered Materials

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Two switchable, mesoscopically periodic materials were created by combining crystalline colloidal array (CCA) self-assembly with the temperature-induced volume phase transition of poly(*N*-isopropylacrylamide) (PNIPAM). Body-centered-cubic CCAs of hydrated, swollen PNIPAM particles Bragg-diffract infrared, visible, and ultraviolet light weakly, whereas arrays of compact shrunken particles diffract efficiently. A tunable diffracting array was also created by embedding a CCA of polystyrene spheres within a PNIPAM hydrogel that swells and contracts with temperature; thus the array lattice constant varies with temperature, and the diffracted wavelength was thermally tunable across the entire visible spectrum. These materials may find applications in many areas of optics and materials science.

Monodisperse, concentrated, highly charged colloidal particles in very low ionic strength liquid media can self-assemble because of electrostatic repulsions to form CCAs (*1–6*). These ordered structures form body-centered-cubic (bcc) or face-centered-cubic arrays with lattice constants in the mesoscale size range (50 to 500 nm). Just as atomic crystals diffract x-rays that meet the Bragg condition, CCAs diffract ultraviolet (UV), visible, and near-infrared (near-IR) light (*7*); the diffraction phenomena from these materials resemble that from opals, which are close-packed arrays of monodisperse silica spheres (*8*). The CCAs, however, can be prepared as macroscopically ordered arrays from non–close-packed spheres where Bragg diffraction is highly efficient. All light meeting the Bragg condition is diffracted, and adjacent spectral regions freely transmit. Such arrays can be used as narrow-band optical diffraction filters (*4, 9–11*) and have been proposed for use in nonlinear optical switching applications (*12–14*).

Asher *et al.* recently proposed that CCA self-assembly could be used as a motif for the synthesis of solid, mesoscopically periodic materials (*15*). Asher and co-workers have developed methods to prepare a hydrogel network around the CCA, which permanently locks in the ordering (*15, 16*). We have now used this approach to create two periodic materials such that either the size or the periodicity of the array can be switched.

We utilized the well-known temperature-induced volume-phase transition of poly(*N*-isopropylacrylamide) (PNIPAM) (*17–19*) to create CCA materials with variable sphere size and array periodicity. In water below ~30°C, PNIPAM is hydrated and swollen, but when heated above its lower critical solution temperature (~32°C), it undergoes a reversible volume phase transition to a collapsed, dehydrated state. The temperature increase causes the polymer to expel water and contract into a more hydrophobic polymer state.

We developed a method of synthesizing monodisperse, highly charged colloidal particles of PNIPAM using methods similar to that of Pelton and co-workers (*20, 21*). Dispersion polymerization at ~70°C yielded collapsed colloidal spheres in the 100-nm size range. These colloidal particles exhibit a volume response to temperature similar to that of conventional macroscopic PNIPAM gels (*22*). For example, the diameter of a typical preparation of PNIPAM colloids is temperature-dependent (Fig. 1); the sphere diameter increases from ~100 nm at 40°C to ~300 nm at 10°C, which corresponds to a 27-fold increase in volume. The turbidity of a dilute unordered dispersion of PNIPAM colloids increases as the sphere diameter decreases at higher temperature (*23, 24*) (Fig. 1).

These PNIPAM colloids self-assemble in deionized water to form CCAs both above and below the polymer phase-transition temperature. The array diffracts light and closely follows [not exactly (*7*)] the Bragg diffraction law

$$m\lambda = 2nd\sin\theta \qquad (1)$$

where m is the order of diffraction, λ is the wavelength of incident light, n is the refractive index of the suspension, d is the interplanar spacing, and θ is the glancing angle between the incident light and the diffracting crystal planes (*7*), which are oriented parallel to the crystal surface in the CCA we prepare. Figure 2 shows the resulting extinction spectra of a PNIPAM CCA at 10° and 40°C. The lattice constant of the bcc array is 342 nm, and the nearest neighbor sphere distance is 242 nm. At low temperatures, the CCA particles are highly swollen, almost touching, and diffract weakly. Above the phase-transition temperature, the particles become compact and

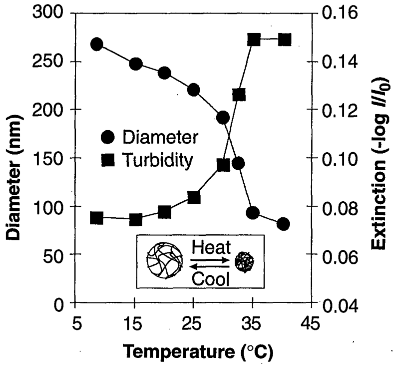

Fig. 1. Temperature dependence of the PNIPAM colloid diameter and turbidity. We determined the diameter by using a commercial quasi-elastic light scattering apparatus (Malvern Zetasizer 4). The turbidity was measured for a disordered dilute dispersion of these PNIPAM colloids by measurement of light transmission through a quartz cell of 1-cm pathlength with a UV–visible–near IR spectrophotometer. The solids content of the sample in the turbidity experiment was 0.071%, which corresponds to a particle concentration of 2.49×10^{12} spheres per cubic centimeter.

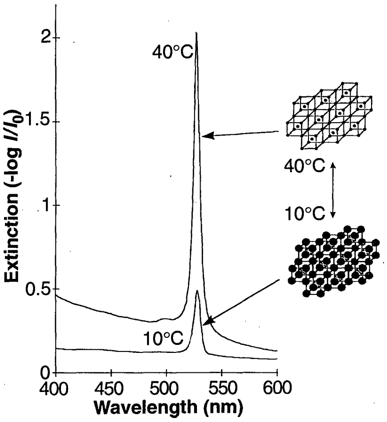

Fig. 2. Diffraction from a CCA of PNIPAM spheres at 10° and at 40°C. We recorded the spectra using a UV–visible–near IR spectrophotometer (Perkin-Elmer λ-9). The dispersion was contained in a 1.0-mm quartz cuvette oriented normal to the incident beam. The observed diffraction switching behavior was reversible; these spectra were recorded after the seventh consecutive heat-cool cycle. (**Inset**) Pictorial representation of the temperature switching between a swollen sphere array below the phase-transition temperature and an identical compact sphere array above the transition.

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diffract nearly all incident light at the Bragg wavelength. The temperature change does not affect the lattice spacing; the 1-nm shift of the maximum wavelength of diffraction upon heating from 10° to 40°C results almost entirely from the change in the refractive index of water.

The diffraction efficiency of CCAs depends on the scattering cross section of the colloidal particles as well as the array ordering. The change in the size of the particles alters the sphere scattering cross section, which in turn markedly changes the diffraction efficiency (*24*). Therefore, this material acts as a thermally controlled optical switch as well as an optical limiter.

We were able to fabricate wavelength-tunable diffraction devices by using the volume phase-transition properties of the PNIPAM gel to control the periodicity of a CCA. We dispersed monodisperse, highly charged polystyrene (PS) spheres in an aqueous solution containing NIPAM monomer. The PS colloid self-assembled into a bcc CCA. We then photochemically initiated NIPAM polymerization to create a CCA embedded in a PNIPAM hydrogel film 125 to 500 μm thick (*25*). This polymerized CCA film (PCCA) shrinks and swells continuously and reversibly between 10° and 35°C; the array of embedded PS spheres follows, changing the lattice spacing and thus the diffracted wavelength.

The diffracted wavelength for the prepared PCCA film could be tuned between 704 and 460 nm by variation in the temperature (Fig. 3). In addition to the change in the diffracted wavelength, the diffraction peak intensity increased as the volume decreased because the diffraction intensity is proportional to the density of scatterers per layer, which increases as the material shrinks (*7*).

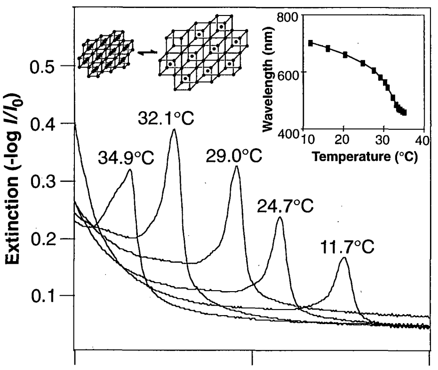

Fig. 3. Temperature tuning of Bragg diffraction from a 125-μm-thick PCCA film of 99-nm PS spheres embedded in a PNIPAM gel. The shift of the diffraction wavelength results from the temperature-induced volume change of the gel, which alters the lattice spacing. Spectra were recorded in a UV–visible–near IR spectrophotometer with the sample placed normal to the incident light beam. The inset shows the temperature dependence of the diffracted wavelength for this PCCA film when the incident light is normal to the (110) plane of the lattice.

This PCCA film functions as an easily controlled tunable optical filter. One can alter the diffracted wavelength by varying either the temperature or the angle of incidence. At a fixed angle to the incident beam, this PCCA acts as a tunable wavelength reflector. The width and height of the diffraction peak can be easily controlled by the use of colloidal particles of different sizes and refractive indices or by the manufacture of PCCA films of different thicknesses (*7*). The tuning range can be widened or narrowed by synthesis of PCCA films with higher or lower cross-linker concentrations.

The two mesoscopic periodic materials that we have fabricated have dimensions that are controllable by temperature; these materials can be used for light modulation in tunable diffracting and transmitting optical devices. They are likely to have additional technological applications for display devices and for image processing. For example, diffraction from these materials can be used to monitor the swelling properties of hydrogels. The diffracted wavelength gives detailed information on the gel volume, and an optical microscope could be used to examine the Bragg diffraction from small areas within the gel film to monitor the phase-transition homogeneity of the gel.

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21. The particles were formed by the dispersion polymerization of 3.47 g of NIPAM (main monomer), 0.03 g of 2-acrylamido-2-methyl-1-propanesulfonic acid (ionic comonomer), 0.105 g of *N,N'*-methylene-*bis*-acrylamide (cross-linker), 0.080 g of SDS (surfactant), and 0.014 g of potassium persulfate (free-radical initiator) in 250 ml of ultrapurified water at 70°C for 4 hours. After synthesis the latex was purified by exhaustive ultracentrifugation and subsequent mixing with mixed-bed ion-exchange resin. The ionic comonomer was added to provide additional surface charge to facilitate CCA formation.
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23. PNIPAM particles have unusual scattering properties because their size and refractive index are intimately related:

$$n_s = n_m\left[1-\left(\frac{r_0}{r}\right)^3\right] + n_p\left(\frac{r_0}{r}\right)^3 \qquad (2)$$

where n_s, n_p, and n_m are, respectively, the sphere, polymer, and medium refractive indices; r is the sphere radius; r_0 is the radius of a completely collapsed, dehydrated sphere; and the ratio $(r_0/r)^3$ represents the size-dependent volume fraction of polymer in the sphere. The Rayleigh-Gans approximation to Mie theory predicts the sphere scattering efficiency to be

$$Q_{\text{ext}} = \frac{32}{27}\left(\frac{n_s}{n_m} - 1\right)^2\left(\frac{2\pi r}{\lambda}\right)^4 = \frac{32}{27}\left(\frac{16\pi^4 r_0^6}{\lambda^4 r^2}\right) \qquad (3)$$

where n_s and r are, respectively, the refractive index and radius of the sphere; n_m is the refractive index of the medium (water); and λ is the wavelength of incident light (*24*). The refractive index factor dominates over the size factor in determining the scattering efficiency, and the scattering decreases approximately as r^{-2}. We determined the scattering cross sections of the PNIPAM colloids by measuring the turbidity of a known concentration of particles. Our calculations of the scattering cross sections based on Rayleigh-Gans theory agree to within 20% of the measured scattering cross sections.
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25. We synthesized the PCCA by photopolymerization of an ordered dispersion of 0.23 g of monodisperse PS colloids (99-nm diameter, 19% solids), 0.35 g of NIPAM (monomer), 0.02 g of *N,N'*-methylene-*bis*-acrylamide (cross-linker), and 0.004 g of diethoxyacetophenone (UV photoinitiator) between two quartz plates separated by a parafilm spacer at ~2.0°C. The diffraction of the polymerized film was similar to that of the monomeric precursor. Careful purification (*15*) of all chemicals and sample cell components are required to achieve CCA self-assembly; a small concentration of ionic impurities will screen the electrostatic repulsive interactions.
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