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Design of Intelligent Mesoscale Periodic Array Structures Utilizing Smart Hydrogel

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Introduction

Mesoscale Periodic Array Structures (MPAS, also known as crystalline colloidal arrays), composed of aqueous or nonaqueous dispersions of self-assembled submicron colloidal spheres, are emerging toward the development of advanced optical devices for technological applications. This is because of their unique optical diffraction properties and the ease with which these intriguing properties can be modulated experimentally.[1] Moreover, our recent advancements in this area which include "locking" the liquid MPAS into solid[2] or semisolid[3] polymer matrices for greater stability with longer life span, and incorporation of CdS quantum dots[4] and laser dyes[5] into colloidal spheres to obtain nonlinear optical (NLO) responses, further corroborate the use of MPAS in optical technology.

Our long term goal is fabrication of all-optical and electro-optical devices such as spatial light modulators for optical signal processing and flat panel display devices by utilizing intelligent nonlinear periodic array structural materials. Recently, NASA is showing an interest in NLO device technology to develop laser communication devices for use in communication satellites deployed in space. Also researchers seek to process materials in microgravity for fundamental studies, and explore the potential of achieving superior performance for device applications. Here we show further progress in the design of novel linear MPAS which have the ability to sense and respond to an external source such as temperature, a step behind the use of a laser as the ultimate source. This is achieved by combining the self-assembly properties of polymer colloidal spheres and thermoshrinking properties of smart polymer gels.[6] At selected temperatures, the periodic array efficiently Bragg diffracts light and transmits most of the light at other temperatures. Hence, these intelligent systems are of potential use as fixed notch filters, optical switches or limiters to protect delicate optical sensors from high intensity laser radiation.

Experimental

We synthesized submicron monodisperse crosslinked(CL) poly(N-isopropylacrylamide) (PNIPAM) hydrogel spheres by dispersion copolymerization of N-isopropylacrylamide and N,N'-methylenebisacrylamide using sodium dodecylsulfate and potassium persulfate at 70 °C following a methodology similar to Pelton *et al*.[7] We added a small amount of ionic comonomer, 3-acrylamido-2-methyl-1-propanesulfonic acid (0.45 mol%/NIPAM) while preparing 3% CL spheres to increase the number of charged groups on the sphere. However, no ionic comonomer was added during the preparation of 10% CL spheres. The colloidal dispersions were extensively purified to remove residual ionic species from the initiator fragments, excess surfactant and soluble polyelectrolytes. The dispersions were ultracentrifuged at least 4 to 5 times at 20000 rpm and 20 °C, and then mechanically stirred with mixed bed ion exchange resin at 40 °C for about 30 min. The ion exchange resin was filtered out and then the dispersions were ultracentriguged to obtain desired concentration.

Results and Discussion

PNIPAM gel is an interesting thermosensitive polymer which exhibits a reversible volume change in aqueous medium at 32 °C, causing many of its physico-chemical properties to change concurrently.[9] The submicron PNIPAM gel spheres also displayed remarkable volume changes around 32 °C. Below the phase transition temperature, the spheres are swollen and are electrosterically stabilized, and above which the spheres are collapsed and are electrostatically stabilized. Figure 1 shows the changes in hydrodynamic particle diameters of 3 and 10 wt% CL gels with increase in temperature. The spheres gradually shrunk in size

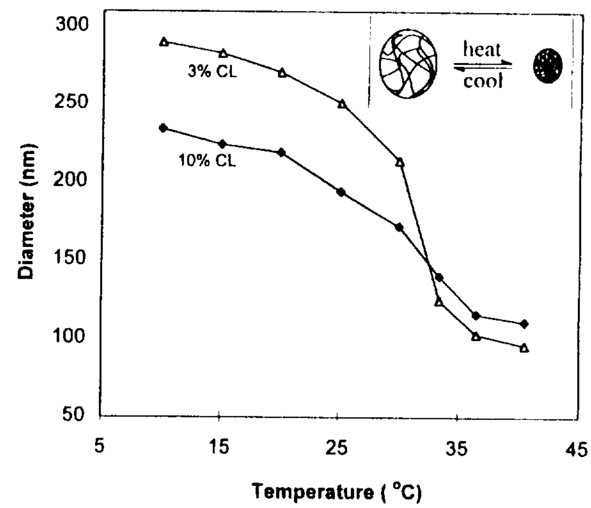

Figure 1. Changes in hydrodynamic sphere diameters of 3 and 10 wt% crosslinked PNIPAM as a function of temperature.

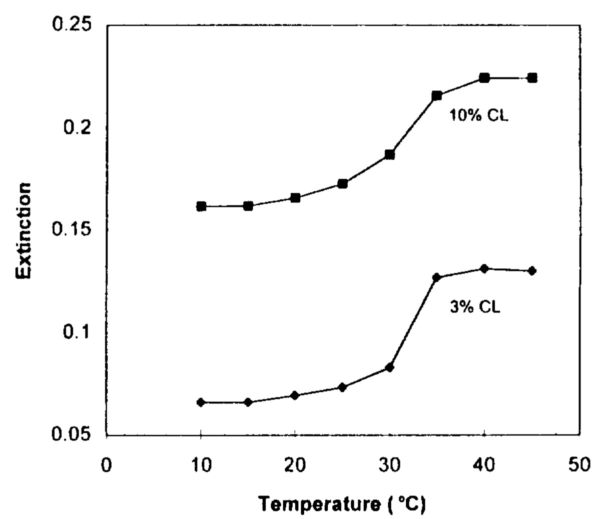

Figure 2. Turbidity measurements of diluted colloidal dispersions of 3 and 10% CL spheres as a function of temperature at 550 nm.

with increase in temperature from 10 to 30 °C and then shrunk very rapidly in the temperature range of 30-35 °C. The 3% CL spheres which were prepared in the presence of ionic comonomer are smaller in diameter and have lower swelling ratio than the spheres prepared with no comonomer. This indicates that the ionic monomer is incorporated into the spheres. Moreover, the phase transition temperature range was narrower for 3% CL spheres than that of 10% CL spheres which may be due to more homogeneous network structures. However, further experiments are needed to confirm our speculations. The reversible change in particle diameter with temperature modulates the volume fraction of the polymer in the spheres which in turn changes the refractive index of the spheres: the index of the spheres is close to the medium when swollen and close to the polymer when they shrink. Figure 2 shows the increase in particle scattering intensities with increase in temperature of the diluted colloidal dispersions. Between the two extreme temperatures studied, the 3% CL spheres exhibited larger scattering intensity ratio than the 10% CL spheres. These results are consistent with the data reported earlier for similar PNIPAM microgel spheres.[8]

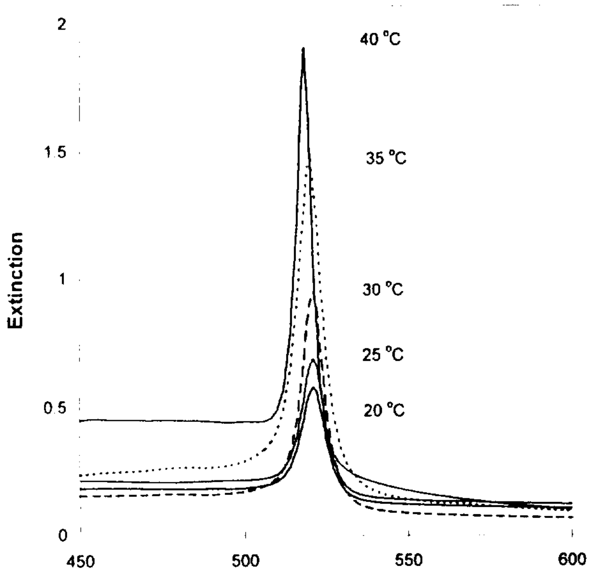

Figure 3 The effect of temperatue on diffraction intensity of MPAS of 3% CL gel spheres in 1mm thick quartz cell. The volume fraction of spheres in the dispersion is 0.02.

MPAS were formed after vigorous purification of the colloidal dispersions and by heating the dispersions around the volume phase transition temperature of the hydrogel. In contrast to conventional polystyrene array dispersions where the spheres self-assemble to large monodomain crystals, a mosaic of polycrystalline microdomains was observed with PNIPAM microgel spheres which may be due to a lower number of charged groups present on the spheres. Figure 3 shows the dramatic optical responses of MPAS of 3% CL microgels as a function of temperature. The diffraction efficiency of MPAS increased remarkably around the phase transition temperature range, 30-40 °C. However, there were no significant changes observed in the diffraction wavelength maximum and peak bandwidths. These results indicate that the temperature only affected the size of the spheres, but the position of the spheres in the lattice is unaltered. Figure 4 compares the diffraction proficiencies of 3 and 10% CL PNIPAM gel structures at two different temperatures (above and below the phase transition temperature). It is obvious from this figure that the low CL system with a large swelling ratio was more efficient in controlling the incident light than the high CL gels. The 3% CL system barely diffracted the incident light at 10 °C, but diffracted the light very effectively above the phase transition temperature, 40 °C. Since the diffraction intensity from the periodic structures is a strong function of index mismatch between the spheres and the medium, the spatial modulation in refractive index of the spheres in the lattice makes this system act as an optical switch at these two temperatures. We observed that the optical responses of MPAS with temperature are highly reversible, and no hysteresis was noticed for the sample after several rapid heat and cool cycles. However, these systems are very sensitive to ionic species; i.e. the optical responses of the system with temperature are not reversible in the presence of minute amounts of soluble polyelectrolytes. Hence care must be taken to purify the dispersions thoroughly to achieve high reproducibility. More efficient systems can be designed by maximizing the sphere's swelling ratio and adjusting the array thickness. These optical responses can also be controlled by laser radiation[10] after incorporating light absorbing chromophore into these hydrogel spheres. Alternatively, NLO materials can be introduced to induce intensity dependent changes in the refractive index of the structures.

We have previously developed solid notch laser filters by embedding arrays of functionalized colloidal silica or polystyrene latex spheres into a variety of polymeric matrices such as thermoplastic (polymethyl methacrylate, PMMA)[2], elastomeric (polymethyl acrylate, PMA)[2] and hydrogels (polyacrylamide, PAM)[1]. In these composite films, MPAS are more environmentally stable than in the traditional liquid films.

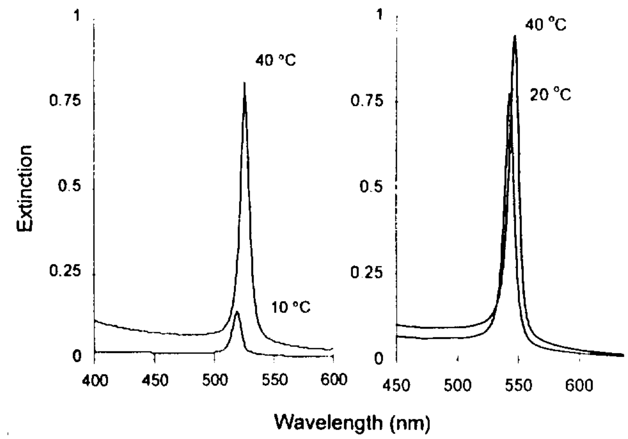

Figure 4. Diffraction intensities from the arrays of 3 (left) and 10% CL spheres (right) between two temperatures (below and above the phase transition). The thickness of the samples is approximately 200 μm.

Among the composite films prepared, the glassy PMMA composite films in which the MPAS were covalently fixed to the matrix appear to be more promising materials for NLO device applications because the films are rigid, easy to handle, and have high laser damage thresholds. However, the optical quality of the solid films is not in the desired range and has to be improved further. We suspect that some of the parameters which might affect the optical quality of the film during crystal growth of silica spheres and subsequent photopolymerization of monomeric dispersions are: polycrystalline microdomains; gravity-driven crystal motion; and buoyancy-driven convection during irradiation. Currently, NASA is investigating fundamental studies of order-disordered phase transitions of colloidal spheres in space, the science from this mission (STS-73) can help us to learn how to grow large crystals of silica in space and to irradiate the samples on orbit to prepare composite films with high optical quality for benchmark materials.

In conclusion, we have created new intelligent periodic arrays with thermosensitive poly(N-isopropylacrylamide) hydrogels; the diffraction efficiencies of the structures can be switched on-off simply by altering the temperature between 10 and 50 °C. These systems will find numerous applications in advanced optical devices. Further experiments are in progress to develop high performance nonlinear periodic array structures.

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