Optically Nonlinear Bragg Diffracting Nanosecond Optical Switches

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(Received 30 December 1996)

Monodisperse, highly charged colloidal particles in low ionic strength solutions self-assemble into bcc or fcc crystalline colloidal arrays (CCAs) due to interparticle repulsive interactions. We demonstrate that a CCA of dyed particles embedded in a poly acrylamide hydrogel acts as a nanosecond optical Bragg diffraction switching device. Under low light intensities the CCA is refractive index matched to the medium and does not diffract. However, high intensity excitation within the dye absorption band heats the spheres within nanoseconds to decrease their refractive index. The array "pops up" to diffract light within 2.5 ns. These intelligent CCA hydrogels may have applications in optical limiting, computing, and nanosecond fast optical switching devices, etc. [S0031-9007(97)03099-8]

Dispersions of highly charged, monodisperse colloidal particles in low ionic strength aqueous solutions self-assemble into crystalline colloidal arrays (CCAs) [1–5] at particle concentrations of $\sim 10^{13} - 10^{14}$ cm^{-3}. These colloidal particles organize into either body centered cubic (bcc) or face centered cubic (fcc) structures, where the volume fraction of colloidal particles is small; the spheres' surfaces can be physically separated by distances greater than their diameters [Fig. 1(a)]. The choice of a bcc or fcc structure depends upon the magnitude of repulsion between nearest neighbors, as well as second and third nearest neighbors. It is easy to determine the crystal structure through studies of their Kossel ring Bragg diffraction patterns [6]. The colloidal particles generally orient such that their highest sphere density planes lie parallel to the container walls; the spheres are strongly attracted to the container walls by image charge interactions [7]. Thus, it is easy to form oriented thin single colloidal crystals between quartz plates, where the fcc (111) plane or the bcc (110) planes are oriented parallel to the quartz plates.

These arrays have spacings such that the bcc (110) and the fcc (111) planes Bragg diffract light in the visible region. We showed that these CCAs diffract all incident light which meets the Bragg condition and that these materials were useful as passive optical filters [5,6,8].

Although these CCAs were easily fabricated for use as Bragg diffraction filters they were inherently unstable; shear forces and mechanical vibrations can transiently disorder these arrays. The CCA elastic modulus is low (~ 100 dyn/cm^2) [9–11]. Further, because the CCA ordering depends upon the electrostatic repulsions between highly charged colloidal particles, any ions leaching into the CCA screen the repulsion and can melt the CCA if they exceed a critical concentration. Thus, long term stability requires highly purified colloids and very clean conditions.

We recently developed methods to polymerize acrylamide hydrogel networks around these CCAs [Fig. 1(b)] to permanently lock in the ordering [12,13]. These polymerized CCAs (PCCAs) are not disordered by vibrations or by addition of ionic impurities. In addition, we recently developed a thermally switchable PCCA of polystyrene colloidal particles polymerized in a poly N-isopropylacrylamide) (PNIAP) hydrogel [14]. This PNIAP-PCCA diffraction is easily tuned by varying the temperature, because the PNIAP hydrogel undergoes a
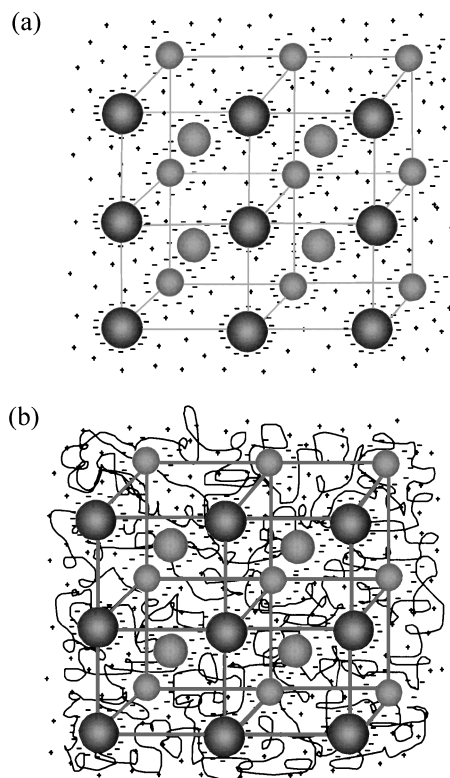
(a)

(b)

FIG. 1. (a) Crystalline colloidal array (CCA) ordering of charged colloidal particle spheres. The CCA is formed by repulsion between the highly charged colloidal particles. The particle charge results from ionization of the numerous surface sulfonate groups. (b) Polymerized CCA (PCCA) formed by polymerization of an acrylamide hydrogel around the CCA lattice.

volume phase transition around room temperature between a swollen and a compact state. This device serves as an efficient tunable optical filter.

These PCCAs permanently lock in the array ordering even though only a relatively small volume fraction consists of colloidal particles and the hydrogel scaffold. These hydrogels permit alteration in the medium surrounding the colloidal particles. For example, we can easily exchange the medium in order to vary the medium refractive index in order to control the diffraction efficiency of the embedded CCA.

In this report we demonstrate that these PCCAs can show optically nonlinear nanosecond switchable diffraction. This demonstration follows our previous theoretical calculation that predicted that CCA made from modestly nonlinear materials could function as efficient nanosecond optical limiting and switching devices [15,16]. The idea was that a CCA does not diffract light when the colloidal particle refractive index is identical to that of the medium. However, if the colloidal particles were optically nonlinear, high intensity illumination would cause a refractive index mismatch between the spheres and the medium; the CCA periodicity would "pop up" to diffract away any light meeting the Bragg condition. At that time we calculated that this optical limiting would occur at fluences of 10 MW/cm^2 within a few nanoseconds when the refractive index mismatch was ~ 0.001. Essentially all of the light meeting the Bragg condition should be diffracted. The nonlinear response results from a thermal nonlinearity in which the spheres contained a dye which absorbed a small fraction of the incident laser light. The sphere heating decreased the sphere density and its refractive index.

Low refractive index, dyed monodisperse colloidal particles were prepared by emulsion polymerization of 10.0 g 1H, 1H-heptafluorobutyl methacrylate (monomer), 0.10 g Aerosol MA 80-I (surfactant), 0.0032 g acylated Oil Blue N (dye) [17], 0.16 g sodium persulfate (free-radial initiator), and 20.0 g deionized water at 55 °C for 3 hours. The colloid was purified by dialysis against ultrapurified water and then put in contact with mixed bed ion exchange resin. The particle diameter (138 nm) was obtained from TEM measurements and the particle charge ($1.0 \ \mu\text{C/cm}^2$) was obtained by measuring the dependence of the suspension conductivity on the particle volume fraction.

These monodisperse highly charged fluorinated colloids have the lowest refractive index ($n_p = 1.3860$) of any monodisperse colloidal spheres known. Such low refractive index colloids are required to easily match their refractive index to that of the medium. We thus can use modest concentrations of a compatible solvent such as DMSO, which has a high dielectric constant (DMSO, $\varepsilon = 45$, $n_D = 1.479$). Acylated Oil Blue N dye absorbs light in the wavelength range of 530 nm and does not fluoresce.

These dyed fluorinated colloids readily self-assembled into a CCA which was polymerized within an acrylamide hydrogel. The PCCA was prepared by photopolymerization of a CCA of 1.58 g monodisperse dyed poly(1H,
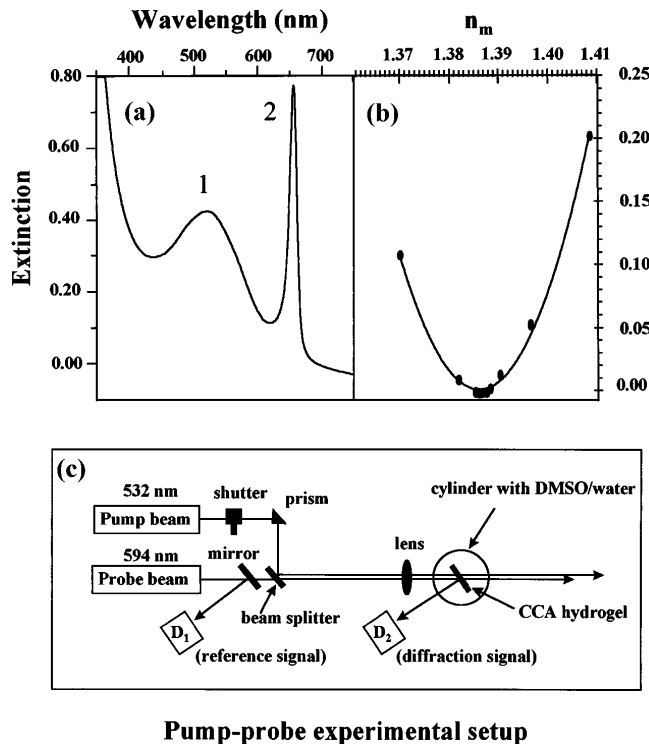
1H-heptafluorobutyl methacrylate) colloid (138 nm in diameter, 11% wt % solids), 1.98 g ultrapure water, 0.345 g acrylamide (monomer), 0.023 g N, N$'$-methylenebisacrylamide (cross-linker), 0.002 g diethoxyacetophenone (UV photoinitiator) between two quartz plates separated by an 800 μm thick parafilm spacer at 25 °C.

DMSO was added to the mainly aqueous medium in order to adjust the medium refractive index (n_m) to be either slightly above or slightly below n_p. The optical extinction spectra of the dyed PCCA is shown in Fig. 2(a). The broad 530 nm band results from the particle dye absorption, while the 640 nm peak results from the CCA diffraction. Figure 2(b) shows the PCCA optical extinction as a function of n_m. An exact refractive index match at $n_m = 1.3860$ causes the CCA diffraction to disappear.

Figure 2(c) shows the experimental setup which monitored the diffraction switching. The 800 μm thick PCCA was oriented in a cylindrical tank containing a water/DMSO mixture. The fcc (111) plane was at the angle ($\sim 20°$) appropriate to Bragg diffract light from a 594 nm probe beam emitted by the dye laser which was pumped by a 532 nm, 3.5 ns pulsewidth YAG laser (Coherent Inc. Infinity). The dye laser probe beam was also of 3.5 nm duration. The 532 nm YAG pump beam was used to switch on the PCCA diffraction. The pump and the probe beams were made collinear and focused into a 100 μm spot size radius on the sample. The probe beam was delayed with respect to the pump by 2.5 ns. Detector 1 monitored the probe beam incident pulse energy while detector 2 monitored the diffracted pulse energy.

Figure 3 shows the dependence of diffraction on the pump beam energy for the PCCA with dyed spheres, with n_m below or above n_p. The plot shows the probe diffracted energy ratio ($R_{\text{on}}/R_{\text{off}}$) in the presence ($R_{\text{on}}$) and absence ($R_{\text{off}}$) of the pump beam. The diffracted energy increases as the PCCA colloidal particles are heated when the initial medium refractive index exceeds that of the spheres [$n_m(1.3902) > n_p(1.3860)$], but the diffracted energy decreases when the initial medium refractive index lies below that of the spheres [$n_m(1.3817) < n_p$]. Laser heating of the spheres where $n_m(1.3902) > n_p(1.3860)$ results in an additional lowering of the sphere refractive index and an increased mismatch from that of the medium. In contrast, a decreased refractive index mismatch occurs for the system where $n_m(1.3817) < n_p$ because the initially higher refractive index spheres decrease their refractive index toward that of the medium. Figure 3 also shows no dependence of the diffracted energy on pump energy for a PCCA without dye.

The diffracted energy from the over- (under-) index matched PCCA shows a dip (peak) around the 600 μJ pump energy region [18]. Above 600 μJ the diffracted energy continues to increase (decrease) until about 1500 μJ. Above 1500 μJ, irreversible damage occurs and destroys the CCA ordering; the diffracted energy decreases for both the over- and under-index matched cases. SEM pictures of the particles after heating in an aqueous suspension by a

Pump-probe experimental setup

FIG. 2. (a) Extinction spectrum of charged 138 nm diameter dyed poly(1H,1H,-heptafluorobutyl methacrylate) PCCA in water. Peak 1 derives from absorption of the acylated Oil Blue N dye which is covalently bounded to the particles; Peak 2 is the PCCA Bragg diffraction band. The spectrum was recorded in a UV-visible–near ir spectrophotometer with the PCCA surface normal to the incident light beam. (b) The optical extinction of the dyed PCA due to diffraction as a function of the medium refractive index. The data (filled circles) are best fit to the parabolic curve: $A = 405.85(n_m - 1.3860)^2 + 0.0063$, where n_m is the medium refractive index and 1.3860 is the colloidal particle refractive index. (c) Pump-probe optical switching experimental setup. An 800 μm thick PCCA was placed in a glass cylinder containing a DMSO/water mixture. The 532 nm pump beam and the 594 nm probe beam both (~3.5 ns duration) were collinear and focused onto the PCCA. The incident probe energy is monitored by the D_1 photodiode while the D_2 photodiode measures the diffracted probe energy. The diffraction switching was monitored at different pump energies and at different optical delay times between the pump and probe.

2000 μJ pump pulse confirm particle damage. The pump beam diffraction dependence in Fig. 3 is completely reversible for pump energies below 1500 μJ.

Further evidence that this behavior results from nonlinear diffraction is that focusing the beams to a smaller spot size decreases the pump energy required to alter the diffraction efficiency. In fact, the pump energy associated with the dip (peak) just after T_g decreases approximately as the square of the spot size radius. When the probe pulse precedes the pump by 2.5 ns, the diffracted intensity does not change. If probe and pump are coincident on the sample at the same time, the signal is only 50% of that observed with a 2.5 ns delayed probe. A probe delay of more than 2.5 ns results in a decrease in the diffraction energy because the PCCA particles start cooling down in this time
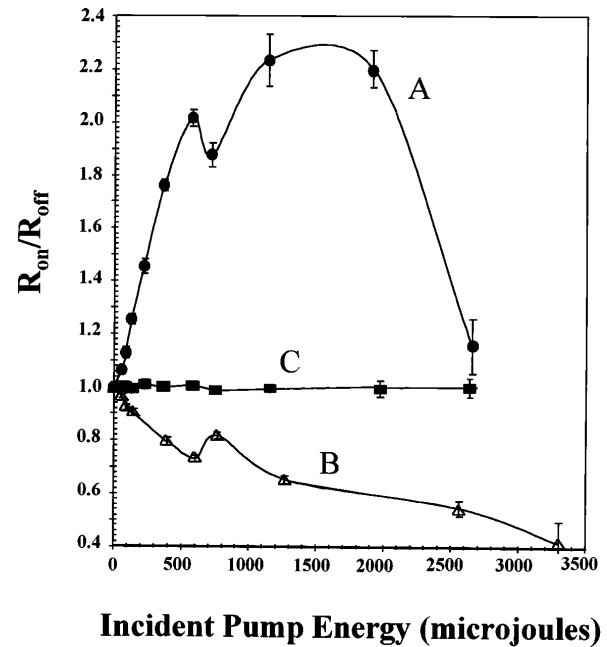

Incident Pump Energy (microjoules)

FIG. 3. Pump beam energy dependence of R_{on}/R_{off} for the case of over- and under-index matching conditions, where the probe beam was delayed by 2.5 ns compared to the pump beam. Curves A and B were measured for a dyed PCCA with n_m adjusted to 1.3902 and 1.3814, respectively. Curve C was measured for an undyed PCCA at $n_m = 1.3874$.

scale [15]. The maximum reversible pump heating of the CAA results in the probe diffraction about 3 times larger than that in the absence of the pump beam.

Thus, we have prepared a nanosecond optical switch which can act as an optical limiter if the dye absorption is coincident with the diffracted wavelength or as an optical switch where a pump beam can control diffraction and transmission of one or many probe beams. This phenomenon may be useful in optical limiting and optical computing devices. In fact, small areas of the array could be individually switched to permit devices for parallel processing. We expect that the density of pixels could be quite high.

At present the device switches only 2% of the probe beam, which is far below that theoretically expected. We calculated using dynamical diffraction theory [6,15,20] that the diffraction efficiency for a perfect PCCA lattice should be 97% for the 600 μJ pump excitation that transiently heats the spheres to 60 °C. Since we independently verified [17] that our temperature and refractive index change conforms with theoretical expectations, we expect that the nonideality results from disorder in the PCCA. We are developing methods to prepare more perfect PCCA films. In addition, we recently discovered that we can increase the sphere scattering power by over ten-fold by using second order diffraction. Further optimization of these PCCA should lead to efficient optical switching devices and limiters. The unique efficiency of these devices results from the fact that the mesoscopic periodicity of the array concentrates the scattering power of

the particles into a narrow solid angle which fulfills the Bragg condition.

We prepared Bragg diffracting crystalline colloidal arrays of dyed poly(1H,1H-heptafluorobutyl methacrylate) spheres of 138 nm diameter locked in an acrylamide hydrogel. We nearly refractively index-matched the particles to the medium and measured the probe diffracted energy change as a function of pump beam heating of this PCCA. We demonstrated that this system acts as a nanosecond switchable diffraction device. The diffracted energy switches sufficiently fast for optical switching and logic devices. Theoretically, over 97% of the incident light should be diffracted. However, we observed a much smaller efficiency due to crystalline colloidal array disorder. We are now in the process of improving the array ordering.

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[18] We directly measured the temperature dependence of our particle specific heat ($1.08 \ \mathrm{J \, K^{-1} g^{-1}}$ at 298 K), and the colloidal particle absorption cross section, in order to calculate the colloidal particle temperature at 600 μJ pump beam energy. This temperature is essentially identical to the T_g value (62 °C) that we determined by differential scanning calorimetry.

The particle specific heat shows an endothermic peak at about 67 °C close to the value of T_g, which probably results from melting of the crystalline portion of this inhomogeneous colloid polymer [19]. The diffraction dip (peak) at around 600 μJ pump energy probably results from this melting, and the consequent particle volume change which results in an increased cooling rate for the spheres, and an increased heating rate for the medium; this abrupt volume change causes liquid turbulent flow of the medium around the particle and causes a small temperature decrease for the particles and a small temperature increase for the medium. Thus, n_p increases and n_m decreases. This causes a decrease (increase) of the index mismatch for the $n_m > n_p$ ($n_m < n_p$) PCCA and results in a dip (peak).

We calculated the pump-induced refractive index mismatch using the measured temperature dependence of n_p ($dn_p/dT = -1.39 \times 10^{-4} \ \mathrm{K^{-1}}$) and the expected particle temperature at the various pump beam energies. We also directly measured the PCCA diffracted intensity for various refractive index mismatches between the particles and the medium, by varying the relative amount of water and DMSO in the PCCA. These measured diffraction intensities are almost identical with those observed (Fig. 3) for pump energies up to ca. 600 μJ pump energies. These values, however, are about 40-fold smaller than that calculated for a perfect PCCA FCC lattice.

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