CRYSTALLINE COLLOIDAL ARRAY OPTICAL SWITCHES AND LIMITERS

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Abstract We fabricated nsec optical switches and optical limiters by utilizing polymerized crystalline colloidal arrays (CCA). CCA are face centered cubic or body centered cubic arrays of colloidal particles with lattice constants of 200-300 nm. These structures efficiently Bragg diffract visible light. We polymerized a CCA of absorbing colloidal particle in a hydrogel matrix and refractive indexed matched the particles to the surrounding medium. Thus, these CCA show a modulation in the only the imaginary part of their refractive index and show little or no diffraction of light. Nsec pulses of visible light absorbed by the colloidal particles increase their temperature which decreases the particle refractive index. This creates a periodic modulation in the real part of the refractive index which pops up in 3 nsec to diffract light. Theoretical calculations indicate that the array should diffract essentially all light meeting the Bragg condition. At present we observe a smaller diffraction efficiency, which is due to disorder in the CCA. We are improving the CCA array ordering to increase the diffraction efficiency.

INTRODUCTION

Dispersions of highly charged, monodisperse, submicrometer size colloidal particles can self-assemble into body centered cubic (bcc) or face centered cubic (fcc) crystalline colloidal arrays (CCA) due to the presence of interparticle screened Coulombic repulsions.[1-6] The refractive index of these particles generally differs from that of the surrounding medium, which results in a periodic variation in the CCA refractive index. This modulation in the refractive index results in Bragg diffraction, similar to the diffraction of x-rays from atomic and molecular crystals. A major difference occurs, however, in that the periodicity in the refractive index for the CCA is much larger than that found for atomic and molecular crystals; it occurs in the 10 nm-3 μm length scale. Thus, the CCA efficiently diffracts electromagnetic radiation in the UV, visible and near-IR spectral regions.[4,6] This unique property can be used to make devices such as narrow band optical rejection filters [4,7-11] and chemical sensing devices.[12]

We demonstrated recently that the CCA periodicity can also be used to fabricate nanosecond nonlinear optical switching and limiting devices.[13-16] The idea is to match the real part of the refractive index of dyed CCA particles to that of the medium. Thus, at low light intensities, no modulation occurs in the real part of the refractive index and light freely transmits. However, since the dyed particles have a thermal nonlinear dependence of their refractive index on the incident light intensity, at high light intensities the particle refractive index diverges from that of the medium, and the periodic modulation of the real part of the refractive index will „pop up" to diffract the high intensity incident light. For a 5 nsec pulsed laser beam of 10 MW/cm^2, our calculations[15] showed that the refractive index of the particles would diverge sufficiently from that of the medium that a perfectly ordered CCA would diffract > 90% of the incident light within 5 ns (Fig. 1).
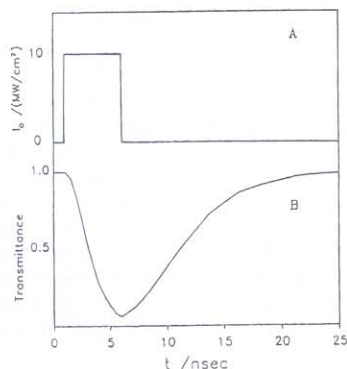

Fig. 1 Calculated time dependence of transmittance through a nonlinear CCA. (A) Temporal dependence of incident heating laser beam. (B) Transmission of probe beam of wavelength 514.5 nm incident at $\theta_B = 75°$ on an indexed matched CCA of 81 nm particles .
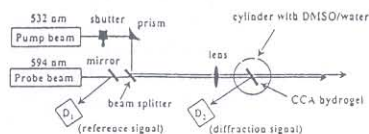

Fig. 2 Experimental setup of nonlinear optical diffraction switching. A PCCA sample was mounted on an aluminum frame, which was placed in a glass cylinder containing a mixture of water and DMSO. The 532 nm pump and 594 nm probe beams (~3.5 ns duration) were collinear and focused onto the PCCA sample. The Bragg diffracted probe intensities were measured by photodiode D_2 and normalized to the incident probe intensity measured by photodiode D_1. R_{off} and R_{on}, the normalized diffracted probe beam, were measured in the absence and presence of the pump beam, respectively. The diffraction switching ratio, R_{on}/R_{off}, was monitored as a function of pump energy.

We developed a synthetic method to fabricate monodisperse, low refractive index, dyed, highly charged colloidal particles consisting of poly(1H,1H-heptafluorobutyl methacrylate)[13]. These particles, have a sufficiently low refractive index ($n_D = 1.3860$) that they can be easily matched to a predominantly aqueous medium. We also covalently attached to these particles the dye Oil Blue N which strongly absorbs light in the 500-540 nm spectral region.

We induced the self assembly of these dyed particles into a CCA which we then polymerized into a polyacrylamide hydrogel matrix (PCCA). We then adjusted the refractive index difference between the particles and the medium by replacing the aqueous medium within the hydrogel. This system allows us to easily fine tune the refractive index mismatch between the particles and the medium.

EXPERIMENTAL

A circular PCCA disc of 1.6 cm diameter was cut and immersed in a water/DMSO solution contained in a cylindrical glass tank. Figure 2 shows the experimental setup used to monitor the diffraction switching. The PCCA surface was tilted from the normal by ~20^0 in order to Bragg diffract a 594 nm probe beam from a dye laser, which was pumped by a 532 nm, 3.5 nsec pulsewidth YAG laser (Coherent Inc. Infinity). The 532 nm YAG pump beam was used to switch on the PCCA diffraction. The pump and the probe beams were collinear and focused onto a 100 μm radius spot on the PCCA sample. The probe beam was delayed with respect to the pump by 2.5 ns. The diffracted probe energy (I_2), as measured by photodiode D_2, was normalized to the incident probe energy (I_1), as measured by photodiode D_1, because the dye laser output fluctuates from one pulse to another by ca. 6%. R_{off} and R_{on}, the normalized diffracted probe beam intensities in the absence and presence of the pump beam, respectively, are defined as:

$$R_{off} = (I_2/I_1)_{off} - (I_2/I_1)_{bck}, \qquad R_{on} = (I_2/I_1)_{on} - (I_2/I_1)_{leakage} - (I_2/I_1)_{bck} \qquad (1)$$

where $(I_2/I_1)_{off}$ and $(I_2/I_1)_{on}$ are the normalized signals in the absence and presence of the pump beam, respectively. $(I_2/I_1)_{leakage}$ is the normalized leakage pump beam signal in the absence of the probe beam, $(I_2/I_1)_{bck}$ is the normalized background signal in the absence of

both the probe and the pump beams.   Each measurement (R_{on}/R_{off}) was averaged over 20 pulses and the standard deviation was calculated.   An absorbing filter placed in front of D_2 removed most of the 532 nm scattered pump beam.   The remaining leakage of the scattered pump beam into D_2 was numerically removed from the measured R_{on} as shown in Equation (1).

RESULTS and DISCUSSION

Figure 3A shows the extinction spectrum of the PCCA in a DMSO/water solution at normal incidence, while Figure 3B shows the dependence of the maximum value of this extinction at 656 nm, as a function of the hydrogel medium refractive index(n_m).   The 530 nm peak results from the dye absorption band.   The diffraction of the incident beam almost follows Bragg law:

$$M \lambda_o = 2 \, n \, d_{hkl} \sin \theta_B \tag{2}$$

where M is the diffraction order, λ_o is the Bragg diffracted wavelength in air. d_{hkl} is the interplanar spacing of the lattice plane with Miller indices (hkl). θ_B is the Bragg glancing
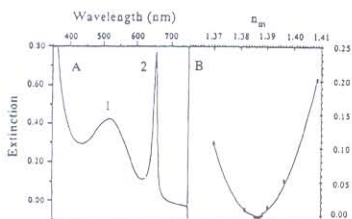

Fig. 3 (A): Extinction spectrum of 138 nm diameter dyed poly(1H,1H-heptafluorobutyl methacrylate) PCCA in water.   Peak 1 derives from absorption of acylated Oil Blue N dye covalently bound to the particles. Peak 2 is the PCCA Bragg diffraction. The spectrum was measured with the PCCA surface normal to the incident light. (B): Extinction of dyed PCCA (sample A) as a function of medium refractive index. The data (filled circles) are best fit to: A = $405.85(n_m - 1.3860)^2 + 0.0063$, where n_m is the medium refractive index and 1.3860 is the particle refractive index.
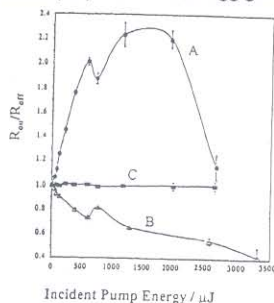
Fig. 4   Pump beam energy dependence of R_{on}/R_{off} for the case of over- and under-index matching conditions.   The probe beam was delayed by 2.5 ns compared to the pump beam.   The pump beam spot size on the sample had a 100 μm radius. Curve A and B were measured for a dyed PCCA with n_m adjusted to 1.3902 and 1.3817, respectively; Curve C was measured for an undyed PCCA at $n_m = 1.38$

angle between the incident beam and the (hkl) plane inside the crystal. n is the average refractive index of the PCCA:

$$n = n_p\Phi_p + n_m(1-\Phi_p) \tag{3}$$

where n_p is the particle refractive index (1.3860). Φ_p is the particle volume fraction in the PCCA. n_m is the hydrogel medium refractive index given by

$$n_m = 1.543x + n_{mix}(1-x) \tag{4}$$

where 1.543 is the refractive index of polyacrylamide. x is the volume fraction occupied by the polyacrylamide hydrogel network in the medium, and n_{mix} is the measured refractive index of the DMSO/water solution. n_{mix} can be varied by varying the fraction, y, of DMSO in water,

$$n_{mix} = 1.479y + 1.333(1-y) \tag{5}$$

where 1.479 and 1.333 are the refractive indices of DMSO and water, respectively. The extinction is defined by:

$$E = -\log(1-\frac{I_D}{I_0}) \tag{6}$$

where I_0 is the incident light intensity, I_D is the diffracted intensity. The extinction was best fit to a parabola:

$$E = a_1(n_m - n_p)^2 + b_1 \tag{7}$$

We found x = 0.0301, a_1= 405.85, b_1 = 0.0063. The minimum value of E occurs when n_m = n_p.

We placed the PCCA in the sample chamber, adjusted the medium to the appropriate refractive index and made the pump and probe beams coincident on the sample. Figure 4 shows the measured ratio of the diffraction of the probe beam in the presence and absence of the pump beam. Curve A was obtained for an over-index matched (n_m(1.3902) > n_p(1.3860)) PCCA, while curve B was obtained for an under-index matched (n_m(1.3817) < n_p(1.3860)) PCCA, and curve C was obtained for an undyed PCCA with n_m = 1.3817. The signal, R_{on}/R_{off}, is independent of the pump energy for the undyed PCCA, since the undyed colloidal spheres do not absorb the pump. Thus, their temperature and n_p do not change; hence, no change occurs in the diffraction efficiency with increasing pump energy.

Curves A and B clearly indicate an optically nonlinear response of the dyed PCCA. As the pump beam heats the CCA, the diffraction efficiency increases when it is over-index matched ($n_m > n_p$), but decreases when it is under index-matched ($n_m < n_p$). The dyed CCA particles absorb the pump energy and heat up to decrease n_p, since $dn_p/dT < 0$. The over-index matched particles show an increasing refractive index mismatch as the pump pulse energy increases, and the particle refractive index decreases; this results in increased diffraction. In contrast, the under index-matched CCA becomes more matched on pump beam heating, which causes the diffraction to decrease.

A measurement of the transmitted pump energy indicates that the particles in the PCCA absorb 34% of the incident pump energy, which is identical to that calculated from the dye absorption at $\lambda = 532$ nm shown in Figure 3A. Assuming that this energy was absorbed uniformly by the CCA particles in the volume illuminated by the pump beam, the temperature increase (ΔT) can be calculated:

$$\Delta T = f_1 f_2 \ \Delta E / m \ C_p \tag{8}$$

where ΔE is the average pump pulse energy. f_1 is the fraction of the incident light energy that enters and is absorbed by the PCCA (34%). f_2 is the energy loss coefficient due to the reflection from the front surface of the container wall (96%). C_p is the heat capacity of the polymer making up the particles. Since the PCCA was tilted from normal by $\sim 20^0$, the illuminated total mass of particles by the pump beam is:

$$m = N \ (\pi \ r^2 \ l_o \ / \cos 20^\circ \ ) \ (\ \pi \ d_o^{\ 3} \ / \ 6 \ ) \tag{9}$$

where r is the pump beam radius at normal incidence on the PCCA and l_o is the PCCA thickness. d_0 is the particle diameter. There is insignificant refraction of light within the sample due to the close matching of the refractive index of the surrounding DMSO/water solution and the PCCA sample. N, the particle concentration ($6.11 \times 10^{13}/cm^3$) was obtained from the calculated value of d_{hkl}, using Equation (2), given the 648 nm measured diffraction wavelength, and that n = 1.3926. By inserting $\Delta E = 570$ µJ, $C_p = 1.15$ J/K/g, r = 100 µm, $l_0 = 800$ µm, and $d_0 = 138$ nm into Equations (8) and (9), the particle temperature increase at an incident pump pulse energy of 570 µJ, which corresponds to the first dip (peak) in curve A (B) of Figure 4, was calculated to be 46 ^{0}C. Hence, the calculated particle temperature was 69 ^{0}C. Both the dip in A, and the peak in B of the diffracted probe energy ratio, R_{on}/R_{off} occurs at 570 µJ. This calculated particle temperature of 69 ^{0}C is close to the 62 ^{0}C measured T_g value for these particles[13].

n_p should continuously decrease with increasing particle temperature. Thus, we interpret the dip (peak) in the Figure 3A (B) curve in the over- (under-) refractive index matched sample at pump energies of ~570 μJ to indicate a region where the pump heating does not continuously increase with increasing pump energy. The fact that this pump energy corresponds to the T_g of the particles, suggests that this phase transition is associated with the phenomenon.

As the pump energy continues to increase the diffracted intensity continues to increase (decrease) after the T_g dip (peak), due to further increases in particle temperature, and further decreases in particle refractive index, up to pump energies of ~1500 μJ. As long as the pump energy is maintained below ~1500 μJ, the PCCA response is fully reproducible and there is no evidence of degradation. However, for pump energies above 1500 μJ, the PCCA undergoes irreversibly damage, which results in irreversible diffraction efficiency decreases for both curves A and B of Figure 3. This irreversible PCCA damage appears to result from damage to the array of particles, since we observe damage to a liquid dispersion of these particles if they are illuminated with 1000 pulses of 2000 μJ pump energy focused to a 100 μm spot radius.

Although we calculated that essentially all of the incident light should be diffracted at pump energies of 10 MW/cm^2, we observe that the biggest R_{on}/R_{off} achieved is only 3.0 at T_g. Without the pump the system is poised to diffract ~0.6% of the probe beam. Thus, only ~2% of the probe beam is diffracted in the presence of the pump.

Figure 5 shows the pump delay time dependence of the diffraction efficiency at a pump beam energy which heats the particles to T_g. If the probe precedes the pump by 2.5 nsec, no change in diffraction occurs compared to that in the absence of the pump beam. If the probe and pump coincide in time, the diffraction increases and continues to increase until the probe is delayed by 2.5 nsec relative to the pump. Further delays cause the diffraction efficiency to decrease, and by a 10 nsec delay little impact of pump heating is observed. The maximum diffraction is observed for a probe delay where there is a maximum temporal overlap between the heating and probe pulses. This ~5 nsec observed time dependence is very similar to that we theoretically predicted.[15]

Thus, we have observed nanosecond optical switching for these mesoscopically periodic arrays. We expect that this switching phenomenon can be used for optical limiting if the dye absorption is coincident with the diffracted wavelength, or for optical switching where a pump beam would control the diffraction and transmission of one or more probe beams. In fact this device could be used for parallel optical switching since small areas of the PCCA could be individually addressed to permit parallel processing. We expect that the pixel density could be quite high.
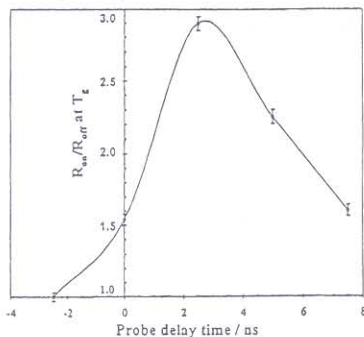

Fig. 5 Dependence of R_{on}/R_{off} on the delay time between the probe and pump beams. The pump beam energy was set to heat the spheres to a temperature of T_g.

At present, however, the device switches only 2% of the probe beam, which is far below that theoretically expected. We calculated using Dynamical Diffraction Theory[9,15,18,19] 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 ^{0}C. Since we independently verified[14] that our temperature and refractive index changes conform to our theoretical conditions, we ascribe the decreased Bragg diffraction efficiency to disorder in the PCCA lattice.

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 10-fold by using second order diffraction.[20] Further optimization of these PCCA should lead to efficient optical switching devices and limiters. The unique potential efficiency of these devices results from the fact that this mesoscopically period array concentrates the scattering power of the particles into a narrow solid angle which fulfills the Bragg condition.

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