OPTICALLY NONLINEAR CRYSTALLINE COLLOIDAL SELF ASSEMBLED SUBMICRON PERIODIC STRUCTURES FOR OPTICAL LIMITERS

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INTRODUCTION

The development of optical technologies requires the fabrication of reliable optical switching and limiting devices. Optical switches modulate the transmission or reflection of incident light, while optical limiters serve to limit transmission to prevent the transmitted light intensity from exceeding a defined level. A major application of optical limiters is to protect delicate sensors.

Various approaches are under investigation for designing optical limiters. Examples include the use of reverse saturable absorbers and the utilization of incident beam heating to drive thermal processes that alter the sample scattering.[1] We are utilizing a unique approach to develop optical limiters which utilizes nonlinear submicron periodic structures to limit transmission by transiently Bragg diffracting away high intensity incident light.[2]

These submicron periodic structures are fabricated by the self assembly of spherical submicron colloidal particles into crystalline colloidal arrays (CCA). This self assembly results from the electrostatic repulsion of surface ionized colloidal particles; these colloidal particles self assemble to form well ordered body centered cubic and face centered cubic crystals[3,4,5] (Fig. 1). The distances between colloidal particles are similar to the wavelength of visible light and these arrays efficiently diffract light meeting the Bragg condition.[6,7] We have fabricated large single crystals which efficiently Bragg diffract away all light that meets the Bragg condition. We recently developed methods to solidify this ordered array by polymerizing a hydrogel network around the array spheres (Fig. 2).[8] The result are solid CCA films which Bragg diffract light and are porous. These films permit the exchange of the fluid medium surrounding the sphere array, while the array ordering is maintained.

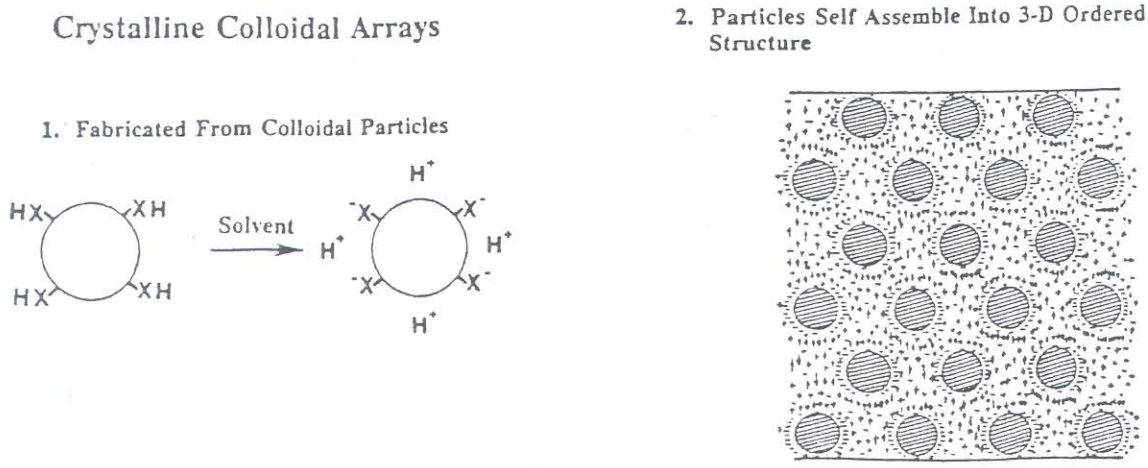

Figure 1. Crystalline colloidal arrays.

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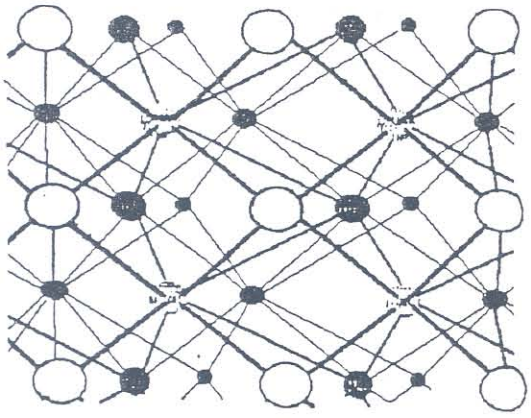

Figure 2. Crystalline colloidal array polymerized in a hydrogel network.

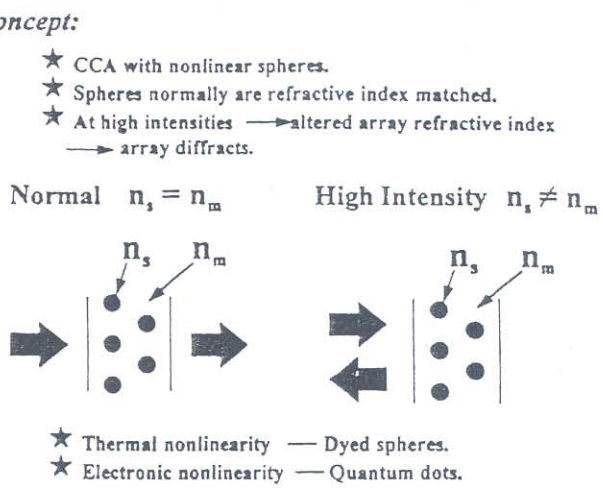

Figure 3. Concept for nonlinear crystalline colloidal array.

CONCEPTS FOR OPTICAL LIMITERS

Our concept for an optical limiter involves creating an array which has the same refractive index as the medium at low intensities, but where the colloidal spheres (or alternatively the medium) have sufficient nonlinearity that at high intensities the sphere array refractive index diverges from that of the medium (Fig. 3). The array "pops up" to diffract the incident light.

The major difficulty with this approach is that a refractive index difference of ca 0.01 is required to achieve sufficient Bragg diffraction; most material nonlinearities are too small to achieve this mismatch at the limiting intensities desired. Two approaches, however, appear possible. We have theoretically examined the utility of thermal nonlinearities, which have the largest n_2 values and have demonstrated that a thermally activated optical limiter could operate and be actuated in the nsec time regime.[9] The idea is to construct a sphere array with dyed spheres which would absorb the laser light and heat up. The refractive index of the sphere array would change sufficiently that the array would "pop up" to diffract away the incident light.

Another similar approach would instead utilize the large electronic nonlinearity of CdS and CdSe quantum dots which have the largest electronic n_2 values known. These quantum dots would be homogeneously incorporated in each of the spheres of the CCA sphere array in order to establish the necessary average nonlinearity required for the sphere array to "pop up" at high light intensities.[10,11]

We have made progress in fabricating both types of nonlinear CCA arrays and report here the development of these new complex submicron periodic structures which will function in novel optical limiters in the near future.

THERMAL NONLINEARITIES

We previously theoretically demonstrated that CCA formed from dyed polymethylmethacrylate spheres would alter their diffraction properties in the nsec time regime[9] (Fig. 4). For example, an incident 5 nsec light pulse of 10 MW/cm^2 will cause the transmission to drop to less than 10% within the 5 nsec pulse width. If the pulse remained on for longer times the transmission would further drop to much lower transmittances (in one design the transmittance is calculated to decrease to 10^{-5} in less than 40 nsec[9]).

The objective is to synthesize colloidal spheres which contain an absorbing dye and which can be refractive index matched to the surrounding medium. This represents a formidable undertaking since most materials have significantly higher refractive indices than water; water is the optimal medium for the self assembly of CCA and for hydrogel film polymerization. Although the hydrogel CCA films permit exchange of the medium with higher refractive index organic solvents, alterations in film dimensions occur at high solvent concentrations which create inhomogeneities in the diffracting films. This results in a degradation in the film diffraction efficiencies.

Our approach has been to use fluorinated polymers which have the lowest refractive indices known for organic compounds. We have developed a new synthesis of ca 50% fluorinated monodisperse colloids which are highly functionalized at the surface with sulfonate groups. The refractive index of these colloids is 1.39, very close to water and easily refractive index matched. Figure 5 shows the diffraction from these CCA as the high refractive index solvent methyl phenyl sulfoxide is added. The Bragg diffraction wavelength increases as the high refractive index solvent is added since the colloid concentration decreases and the lattice spacing increases. The diffraction efficiency decreases as the refractive index of the spheres approach that of the media. No diffraction occurs at the match point, but diffraction returns after the spheres become overmatched. We have also developed a synthetic methodology which allows us to covalently attach the dye Oil Blue N (Fig. 6) and have polymerized this dyed low refractive index CCA in a hydrogel film. We are in the process of determining the intensity dependence of the Bragg diffraction.

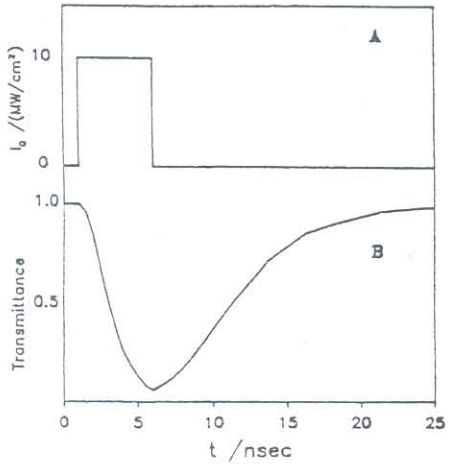

Figure 4. Time dependence of transmittance through a nonlinear optical switch. (A) Heat beam pulse shape. (B) Transmission of the probe beam of wavelength 514.5 nm incident at θ_B =75° on an index matched dyed colloidal crystal of 83 nm diameter PMMA particles as a function of time.

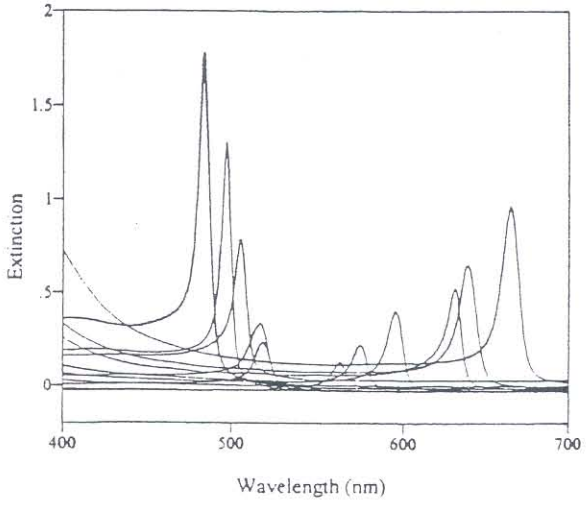

Figure 5. Transmission spectra of fluorinated CCA as a function of the refractive index difference between the spheres and the medium.

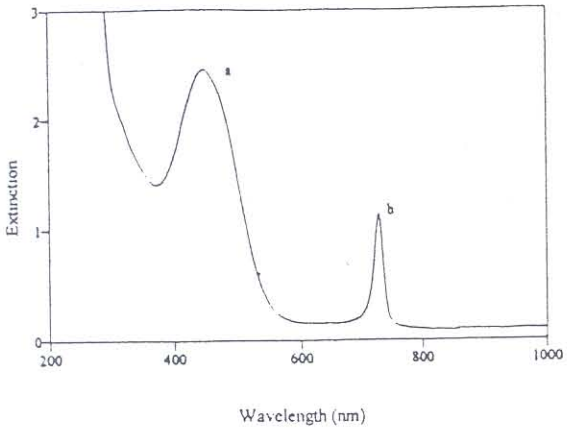

Figure 6. Transmission spectrum of a dyed low refractive index fluorinated CCA. In the figure, peak a results from dye absorption band, while peak b results from Bragg diffraction. The particles were made by copolymerization of 1,1-heptafluorobutyl methacrylate and acylated Disperse Red dye. The CCA particle diameter is 193 nm.

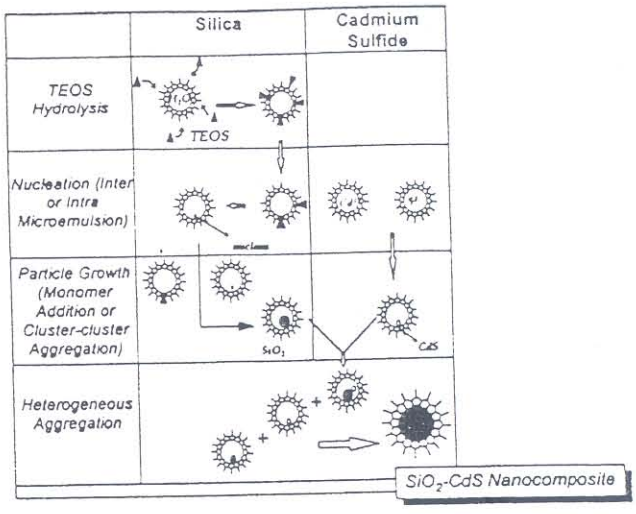

Figure 7. Synthesis of SiO_2-CdS nancomposite.

CdS Quantum Dot Nonlinearities

The objective is to synthesize colloidal spheres containing a large concentration of CdS quantum dots. These quantum dots would be dispersed in ca 100 nm diameter colloidal particles which would be functionalized on their surfaces by strong acid groups. These spheres would self assemble into CCA where the array would be polymerized into a hydrogel film. The refractive index of the colloidal particles would be refractive index matched such that under normal illumination they would not diffract, but at high incident intensities the optical nonlinearities of the quantum dots would cause the average sphere refractive index to diverge from the medium; the array would diffract the incident light away. We have calculated that we will require a concentration of ca 8% by weight of the quantum dots to achieve the necessary average sphere nonlinearity. This system would be among the most complex chemical structure ever fabricated.

We have developed a novel method to synthesize SiO_2 spheres with homogeneously distributed CdS quantum dots.[10,11] Figure 7 shows the mechanism of the synthesis of these nanocomposite spheres in an oil in water microemulsion. Tetraethoxysilane is condensed in the microemulsion microreactor droplets, while Cd^{+2} and S^{-2} ions are added and coprecipitate. Figure 8 shows TEM photographs of these SiO_2-CdS nanocomposite spheres with 5 nm CdS quantum dots, while Figure 9 shows the absorption spectrum and demonstrates the blue shifted band edge associated with homogeneously dispersed ca 2.5 nm quantum dots. X-ray diffraction peak width measurements confirm the quantum dot size.[10]

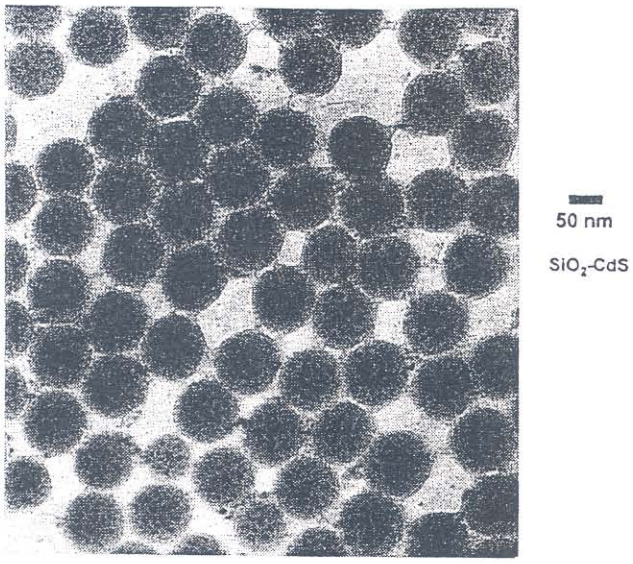

Figure 8. Optically nonlinear colloidal SiO^2-CdS nanocomposite: We have synthesized the nanocomposites in an unique W/O microemulsion As shown above, the monosize nanocomposite is 110 nm in diameter with ~5 nm CdS dots homogeneously dispersed inside.

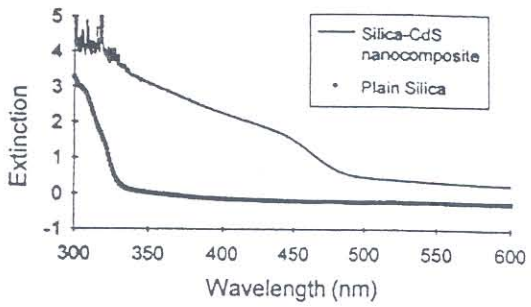

Figure 9. Quantum confinement of 2.5 nm CdS-SiO_2 nanocomposite.

We have functionalized the surface of these colloidal particles with silating agents with sulfonates and demonstrated the self assembly of these highly charged spheres to form well ordered CCA, which we have polymerized in hydrogel films (Fig. 10). We are now measuring the nonlinearities of these arrays.

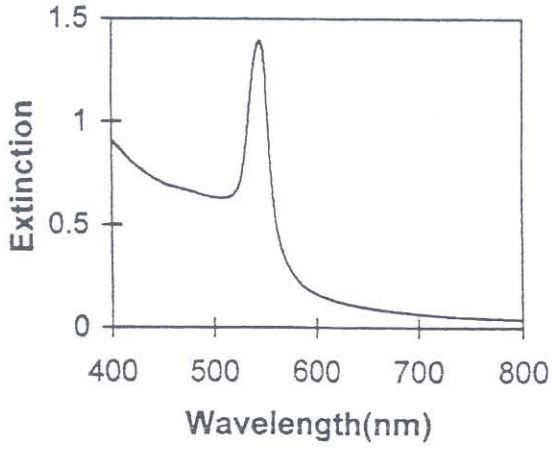

Figure 10. UV-visible spectrum of SiO_2 crystalline colloidal arrays in a polymerized hydrogel film.

SUMMARY

We have made major progress in the demonstration of a new approach to construct optical limiters. We have developed the synthetic methodologies to synthesize and fabricate the thermally and electronically nonlinear periodic submicron structures required for building these devices.

ACKNOWLEDGMENTS

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REFERENCES

1. See the accompanying papers in this symposium volume.
2. S. A. Asher, R. Kesavamoorthy, S. Jagannathan, P. Rundquist, SPIE Vol. 1626 Nonlinear Optics III, 238-241 (1992).
3. P. L. Flaugh, S. E. O'Donnell, and S. A. Asher, Appl. Spectrosc. **38**, 847-850 (1984).
4. R. J. Carlson and S. A. Asher, Appl. Spectrosc. **38**, 297-304 (1984).
5. J. C. Zahorchak, R. Kesavamoorthy, R. D. Coalson, and S. A. Asher, J. Chem. Phys. **96**, 6873-6879 (1992).
6. P. A. Rundquist, P. Photinos, S. Jagannathan, and S. A. Asher, J. Chem. Phys. **91**, 4932-4941 (1989).
7. S. A. Asher, P. L. Flaugh and G. Washinger, Spectroscopy **1**, 26-31 (1986).
8. S. A. Asher, J. Holtz, L. Liu, and Z. Wu, J. Am. Chem. Soc. **116**, 4997-4998 (1994).
9. R. Kesavamoorthy, M. S. Super, and S. A. Asher, J. Appl. Phys. **71**, 1116-1123 (1992).
10. S.-Y. Chang, L. Liu, and S. A. Asher, J. Am. Chem. Soc. **116**, 6739-6744 (1994).
11. S.-Y. Chang, L. Liu, and S. A. Asher, J. Am. Chem. Soc. **116**, 6745-6747 (1994).