

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE September 13, 1996	3. REPORT TYPE AND DATES COVERED Technical Report 01Mar94 to 30Nov96
----------------------------------	--------------------------------------	-------------------------------------------------------------------------

4. TITLE AND SUBTITLE Crystalline Colloidal Array Optical Switching Devices	5. FUNDING NUMBERS C:N00014-94-1-0592 Kenneth J. Wynne R&T code 3132113ess
------------------------------------------------------------------------------------	-----------------------------------------------------------------------------------------

6. AUTHOR(S) S. A. Asher and G. Pan	
--------------------------------------------	--

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Pittsburgh Department of Chemistry Pittsburgh, PA 15260	8. PERFORMING ORGANIZATION REPORT NUMBER No. 4
---------------------------------------------------------------------------------------------------------------------------------------	-------------------------------------------------------

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research-Physical S&T Division, ONR 331 Department of the Navy Arlington, VA 22217-5000	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	------------------------------------------------

11. SUPPLEMENTARY NOTES

Accepted for published in the Proceedings of the NATO Advanced Research Workshop on Nanoparticles in Solids and Solutions.

12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.	12b. DISTRIBUTION CODE
----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	------------------------

13. ABSTRACT (Maximum 200 words)

We have constructed nonlinear crystalline colloidal arrays from self assembling fluorinated colloidal particles which contain dyes. These colloidal arrays were refractive index matched to the medium such that they do not diffract light. We have observed for the first time the theoretically predicted nonlinear diffraction switching when a pump laser beam is incident at a wavelength absorbed by the dye. The colloidal particle array heats up. The refractive index diverges from that of the medium, and diffracts a probe beam.

DTIC QUALITY INSPECTED 2

14. SUBJECT TERMS	15. NUMBER OF PAGES 5
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL
-------------------------------------------------------	----------------------------------------------------------	---------------------------------------------------------	----------------------------------

OFFICE OF NAVAL RESEARCH

Grant N00014-94-1-0592

R&T Code 3132113ess

Technical Report No. 4

Crystalline Colloidal Array Optical Switching Devices

by

S. A. Asher and G. Pan

Accepted for Publication

in the

*Proceedings of the NATO Advanced Research Workshop
on Nanoparticles in Solids and Solutions*

University of Pittsburgh
Department of Chemistry
Pittsburgh, PA

September 13, 1996

Reproduction in whole or in part is permitted for any purpose of the
United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.

19961001 047

CRYSTALLINE COLLOIDAL ARRAY OPTICAL SWITCHING DEVICES

S. A. ASHER and GUISHENG PAN

*Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260*

1. Introduction

Crystalline colloidal arrays are mesoscopically periodic materials which efficiently diffract light meeting the Bragg condition.¹⁻⁴ These materials consist of arrays of colloidal particles which self assemble in solution into BCC or FCC crystalline arrays⁵ (Fig. 1). This self assembly is the result of electrostatic repulsions between colloidal particles, each of which have significant numbers of charged surface functional groups. We have concentrated on the development of crystalline colloidal arrays⁶⁻⁹ which, diffract light in the visible spectral region, and have generally utilized colloidal particles of ca. 100 nm diameter. These particles have thousands of charges, which result from the ionization of sulfonate groups attached to the particle surface. The nearest neighbor distances are ca. 200 nm.

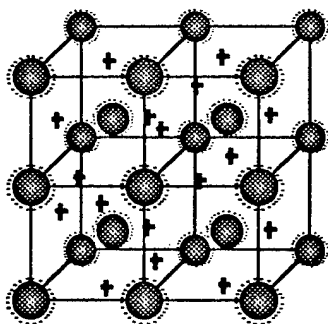


Fig. 1 Crystalline colloidal array composed of a BCC array of negatively charged colloidal particles. The colloidal particle charge derives from ionized surface sulfonate groups. The counterions in the surrounding medium keep the system neutral.

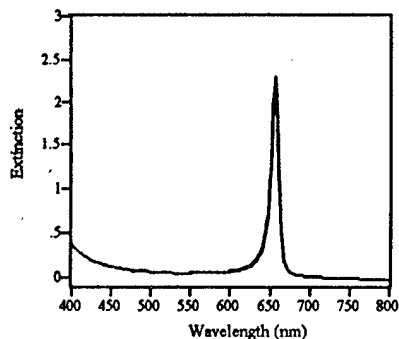


Fig. 2 Transmission spectrum of a 1.0 mm thick crystalline colloidal array formed from 131 nm diameter poly(heptafluorobutyl methacrylate) particles. The particle volume fraction was 6.13%.

These BCC or FCC cubic arrays are well ordered and the arrays strongly diffract light in the visible spectral region (Fig. 2). We earlier demonstrated^{2,3} the use of these devices as optical filters. We more recently developed methods¹⁰ to solidify and rigidize these arrays by imbedding the cubic lattice in a hydrogel polyacrylamide lattice (Fig. 3). This system can be prepared such that the acrylamide and the colloidal array occupy a small percent of the sample volume; most of the volume consists of water. The medium surrounding the spheres can be modified since other solvents can be diffused around the array to replace the water. Although the hydrogel linked crystalline colloidal array shows swelling and shrinkage as the solvent medium is changed, the array ordering is maintained. Films of this array can be prepared where the 110 plane of the BCC lattice is well oriented and parallel to the surface. The 110 planes of the periodic colloidal structure in the film will strongly diffract light meeting the Bragg condition.

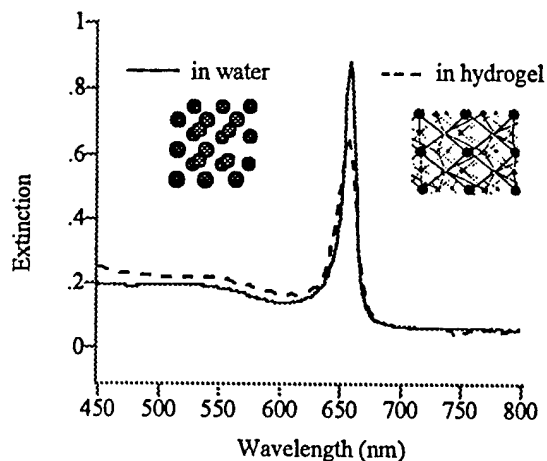


Fig. 3 Transmission spectra of 155 nm diameter poly(heptafluorobutyl methacrylate) crystalline colloidal array before and after solidification in a polyacrylamide hydrogel matrix.

We earlier suggested that we could build nonlinear optical switching materials¹¹⁻¹⁶ by creating an array consisting of polymer spheres containing dye. We would adjust the composition of the medium such that the real part of the refractive index of the spheres was identical to that of the medium.¹⁷ Thus, the array would not diffract light which meets the Bragg condition. However, at high incident light intensities, significant heating would occur within the colloidal particles, the temperature would increase, the refractive index would decrease, and the array would "pop up" to diffract light. We calculated that this onset of diffraction could occur within 5 nsec with pulsed laser sources.¹¹

We demonstrate here the first observation of this nonlinear diffraction phenomenon.

2. Experimental

Monodisperse colloidal particles of a highly fluorinated monomer were prepared with a diameter of 138 nm. These spheres were copolymerized with an acylated Oil Blue N polymerizable dye. The refractive index of these spheres was 1.393, which is lower than that of any monodisperse colloids previously reported. The synthetic methodology will be reported elsewhere.

These colloids self assembled into a crystalline colloidal array which was polymerized within an acrylamide hydrogel. Dimethylsulfoxide was added to the mainly aqueous medium in order to adjust the medium refractive index to the appropriate value either slightly above or slightly below that of the colloidal particles.

Diffraction from the array was monitored using the experimental apparatus shown in Figure 4. The 532 nm pump beam derived from a Coherent Radiation Infinity YAG laser. The probe beam derived from a dye laser pumped by this YAG. The pump and the probe beams were of ca. 3 nsec duration, and were made coincident on the sample, but the probe beam was adjusted temporally such that it was delayed by ca. 3 nsec compared to the pump beam. The relative angle of the sample to the pump beam was adjusted such that the Bragg condition was met. If the refractive index were exactly matched no diffraction should be observed in the absence of the pump beam. If the refractive index of the colloidal particles were adjusted to be slightly greater or less than that of the medium, a very small fraction of the probe beam will diffract.

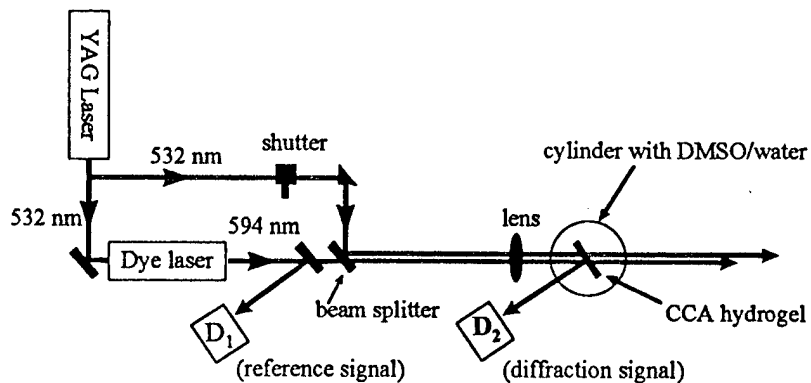


Fig. 4 Schematic of the experimental apparatus for optical nonlinear diffraction measurements.

3. Results and Discussion

Figure 5 shows the extinction spectrum of this dyed crystalline colloidal array hydrogel film measured at normal incident. The broad band centered around 520 nm

results from dye absorption from the colloidal particles. The peak at ca. 640 nm results from Bragg diffraction by the BCC 110 plane.

The film was oriented such that its normal made an angle of ca. 15° relative to the incident beam, so that light at the dye laser output at 594 nm would be diffracted. Figure 6 shows two measurements where the medium has a refractive index of either 1.4045 or 1.3610, which is either above or below the sphere refractive index, respectively. Figure 6 plots the relative value of the diffracted light intensity at various pump energy values compared to the value in the absence of the pump laser.

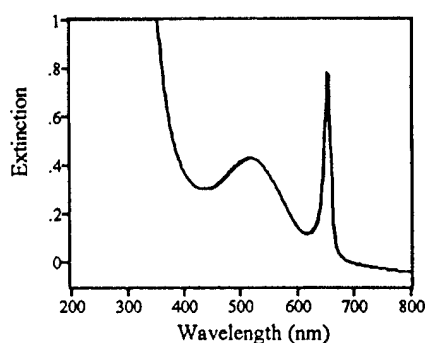


Fig. 5 Transmission spectrum of 138 nm dyed poly(heptafluorobutyl methacrylate) crystalline colloidal array solidified in a polyacrylamide hydrogel matrix.

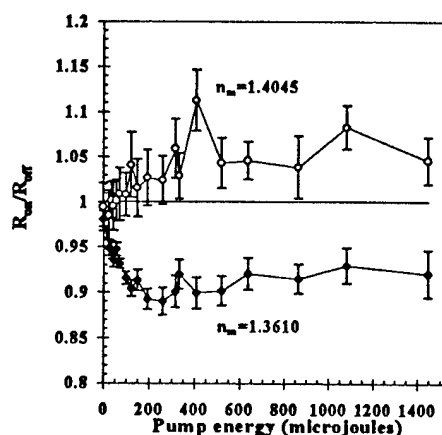


Fig. 6 Pump beam energy dependence of Bragg diffraction intensity. The relative value of Bragg diffraction intensities (R_{on}/R_{off}) were monitored at various pump beam energies.

As expected, if the colloid refractive index is below the medium, heating by the incident beam lowers the colloid refractive index and the diffracted intensity increases. In contrast, if the colloid refractive index is above that of the medium, pump beam heating decreases the refractive index mismatch and the resulting diffraction.

4. Conclusions

We have observed for the first time optical switching in the 3 nsec time regime from an absorbing crystalline colloidal array, as previously theoretically predicted.¹¹ We are continuing to optimize these materials for optoelectronic applications.

Acknowledgment. The authors gratefully acknowledge financial support from the Air Force Office of Scientific Research through Grant No. F49620-93-1-0008, Office

of Naval Research through Grant No. N00014-94-1-0592, and from the University of Pittsburgh Materials Research Center through the Air Force Office of Scientific Research Grant No. AFOSR-91-0441.

References

1. Carlson, R. J. and Asher, S. A. (1984) Characterization of optical diffraction and crystal structure in monodisperse polystyrene colloids, *Appl. Spectrosc.* **38**, 297-304.
2. Flaugh, P. L., O'Donnell, S. E., and Asher, S. A. (1984) Development of a new optical wavelength rejection filter: Demonstration of its utility in Raman spectroscopy, *Appl. Spectrosc.* **38**, 847-850.
3. Asher, S. A., Flaugh, P. L., and Washinger, G. (1986) Crystalline colloidal Bragg diffraction devices: The basis for a new generation of Raman instrumentation, *Spectrosc.* **1**, 26-31.
4. Rundquist, P. A., Photinos, P., Jagannathan, S., and Asher, S. A. (1989) Dynamical Bragg diffraction from crystalline colloidal arrays, *J. Chem. Phys.* **91**, 4932-4941.
5. Zahorchak, J. C., Kesavamoorthy, R., Coalson, R. D., and Asher, S. A. (1992) Melting of colloidal crystals: A Monte Carlo study, *J. Chem. Phys.* **96**, 6874-6879.
6. Rundquist, P. A., Jagannathan, S., Kesavamoorthy, R., Brnardic, C., Xu, S., and Asher, S. A. (1991) Photothermal compression of colloidal crystals, *J. Chem. Phys.* **94**, 711-717.
7. Kesavamoorthy, R., Jagannathan, S., Rundquist, P. A., and Asher, S. A. (1991) Colloidal crystal photothermal dynamics, *J. Chem. Phys.* **94**, 5172-5179.
8. Rundquist, P. A., Kesavamoorthy, R., Jagannathan, S., and Asher, S. A. (1991) Thermal diffuse scattering from colloidal crystals, *J. Chem. Phys.* **95**, 1249-1257.
9. Rundquist, P. A., Kesavamoorthy, R., Jagannathan, S., and Asher, S. A. (1991) Collective diffusion in colloidal crystals, *J. Chem. Phys.* **95**, 8546-8551.
10. Asher, S. A., Holtz, J., Liu, L., and Wu, Z. (1994) Self assembly motif for creating submicron periodic materials. Polymerized crystalline colloidal arrays, *J. Am. Chem. Soc.* **116**, 4997-4998.
11. Kesavamoorthy, R., Super, M. S., and Asher, S. A. (1992) Nanosecond photothermal dynamics in colloidal suspension, *J. Appl. Phys.* **72**, 1116-1123.
12. Asher, S. A., Kesavamoorthy, R., Jagannathan, S., and Rundquist, P. (1992) New nonlinear Bragg diffraction devices, *SPIE Vol. 1626 Nonlinear Optics III*, 238-241.
13. Asher, S. A., Tse, A., Liu, L., Pan, G., Wu, Z., and Li, P. (1995) Optically nonlinear crystalline colloidal self assembled submicron periodic structures for optical limiters, *Mat. Res. Soc. Symp. Proc.* **347**, 305-310.
14. Chang, S.-Y., Liu, L., and Asher, S. A. (1994) Preparation and properties of tailored morphology, monodisperse colloidal silica-cadmium sulfide nanocomposites, *J. Am. Chem. Soc.* **116**, 6739-6744.
15. Chang, S.-Y., Liu, L., and Asher, S. A. (1994) Preparation and processing of monodisperse colloidal silica-cadmium sulfide nanocomposites, *Mat. Res. Soc. Symp. Proc.* **346**, 875-880.
16. Chang, S.-Y., Liu, L., and Asher, S. A. (1994) Creation of templated complex topological morphologies in colloidal silica, *J. Am. Chem. Soc.* **116**, 6745-6747.
17. Tse, A., Wu, Z., and Asher, S. A. (1995) Synthesis of dyed monodisperse poly(methyl methacrylate) colloids for the preparation of submicron periodic light absorbing arrays, *Macromolecules* **28**, 6533-6538.