J. Am. Chem. Soc. 1994, 116, 4997–4998

Self-Assembly Motif for Creating Submicron Periodic Materials. Polymerized Crystalline Colloidal Arrays

Sanford A. Asher,* John Holtz, Lei Liu, and Zhijun Wu

Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received January 24, 1994

We report the development of a method for creating new submicron periodic materials. These materials will have numerous applications in various areas of technology. This periodic material is composed of a body-centered cubic (BCC), face-centered cubic (FCC), or random hexagonal stacked array of spherical particles in which the periodicity is locked into a hydrogel polyacrylamide network.[1] The lattice constant of this array can be varied between *ca.* 10 nm and >1 μm. The particles are generally monodisperse polymer or inorganic spheres with diameters smaller than the lattice constant of the array. The volume percent of particles can be made as large as *ca.* 75% or smaller than 1%.

The periodic array forms through the electrostatic self-assembly of charged colloidal particles. It is well-known that submicron periodic ordered structures called crystalline colloidal arrays (CCA) will self-assemble from monodisperse colloidal spheres containing surface functional groups that ionize in solution.[2-5] If these spheres are dispersed in a polar medium such as water, the surface groups ionize to form spherical macroions which are surrounded by a diffuse counterion cloud. If the solution medium is pure and contains few other ionic species, the repulsive interaction between spherical macroions can be significant over macroscopic distances greater than 1 μm.[6-8] For high particle concentrations ($>10^{13}/\text{cm}^3$) significant interparticle repulsion occurs at the average interparticle spacing; the minimum energy configuration for the assembly of spherical macroions is a BCC or FCC crystal structure.

Monodomain CCA arrays can be made very large; these well-ordered crystalline arrays efficiently Bragg diffract light.[2] Our group has developed techniques to grow large, thin single crystals of these arrays for use as Bragg diffraction devices.[2,9] For example, Figure 1 shows diffraction from a CCA composed of 150-nm polystyrene spheres with a particle concentration of 9.4×10^{13} spheres/cm^3, which corresponds to a volume fraction of 8.3%. These spheres were made by emulsion polymerization of styrene with divinylbenzene as a cross-linker and the sodium salt of 1-(allyloxy)-2-hydroxypropanesulfonate (COPS-1) as an ionic monomer. Each sphere contains 7600 ionizing sulfonate groups. The Bragg diffraction at 525 nm occurs in the dynamical diffraction regime and almost follows the classical Bragg's law:[9]

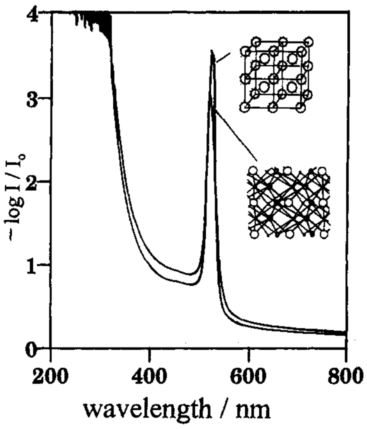

Figure 1. Extinction spectra of a liquid crystalline colloidal array (CCA) and a polymerized crystalline colloidal array (PCCA). The CCA and PCCA were composed of 150-nm polystyrene spheres with surface sulfonate groups in a liquid medium containing 50% *N*-vinylpyrrolidone, 17% acrylamide, 4.5% *N,N'*-methylenebis(acrylamide), and 1% benzoin methyl ether. The similarity of the diffraction peaks of the CCA and the PCCA indicates that little disturbance of the array occurred upon polymerization. The refractive index of the system is *ca.* 1.44.

$$\lambda_0 = 2nd \sin \theta$$

where λ_0 is the wavelength of light in vacuum, n is the refractive index of the system, d is the plane spacing, and θ is the Bragg glancing angle.

These liquid-phase CCA are stable, but will transiently disorder under shock. The CCA will also disorder upon introduction of ionic impurities which screen the interparticle repulsive interactions. Thus, their long-term stability depends upon the cleanliness of their environment and their containers.

We have developed an approach to permanently lock in the CCA array ordering in a solid matrix. We introduce into the CCA highly purified nonionic polymerizable monomers that can form a hydrogel network around the CCA spheres. For example, we form a solid CCA matrix by introducing highly purified acrylamide, *N,N'*-methylenebis(acrylamide), and *N*-vinylpyrrolidone into the CCA solution, and we use UV light to excite benzoin methyl ether to initiate the polymerization.

This liquid polymerized CCA (PCCA) forms a solid hydrogel which locks in the CCA periodic order; the CCA will remain stable in the presence of these polymerizable species provided that the monomers do not contain ionic impurities. The CCA polymerization results in only modest changes in the CCA ordering as evidenced by the modest alterations of the diffraction peak (Figure 1). The hydrogel film is very stable; addition of solutes does not perturb the array ordering since the lattice order no longer depends upon electrostatic interactions between spheres.

The PCCA hydrogel film formed is elastic and contains 30 vol % water. Stretching the gel causes the diffraction peak wavelength to decrease in response to a decrease in the layer spacing;[10] the layer spacing along the film normal decreases as the film is stretched (Figure 2).

---

* Author to whom correspondence should be sent.

[1] Asher, S. A.; Jagannathan, S. U.S. Patent 5,281,370, 1994.

[2] (a) Asher, S. A. U.S. Patents 4,627,689, 4,632,517. (b) Kesavamorthy, R.; Jagannathan, S.; Rundquist, P. A.; Asher, S. A. *J. Chem. Phys.* **1991**, *94*, 5172–5179. (c) Rundquist, P. A.; Kesavamoorthy, R.; Jagannathan, S.; Asher, S. A. *J. Chem. Phys.* **1991**, *95*, 1249–1257. (d) Kesavamoorthy, R.; Tandon, S.; Xu, S.; Jagannathan, S.; Asher, S. A. *J. Colloid Interface Sci.* **1992**, *153*, 188–198. (e) Rundquist, P. A.; Jagannathan, S.; Kesavamoorthy, R.; Brnardic, C.; Xu, S.; Asher, S. A. *J. Chem. Phys.* **1990**, *94*, 711–717. (f) Carlson, R. J.; Asher, S. A. *Appl. Spectrosc.* **1984**, *38*, 297–304. (g) Asher, S. A.; Flaugh, P. L.; Washinger, G. *Spectroscopy* **1986**, *1*, 26–31. (h) Flaugh, P. L.; O'Donnell, S. E.; Asher, S. A. *Appl. Spectrosc.* **1984**, *38*, 847–850.

[3] (a) Krieger, I. M.; O'Neill, F. M. *J. Am. Chem. Soc.* **1968**, *90*, 3114. (b) Hiltner, P. A.; Krieger, I. M. *J. Phys. Chem.* **1969**, *73*, 2386–2389. (c) Hiltner, P. A.; Papir, Y. S.; Krieger, I. M. *J. Phys. Chem.* **1971**, *75*, 1881–1836.

[4] (a) Clark, N. A.; Hurd, A. J.; Ackerson, B. J. *Nature* **1979**, *281*, 57–60. (b) Ackerson, B. J.; Clark, N. A. *Phys. Rev. Lett.* **1981**, *46*, 123. (c) Aastuen, D. J. W.; Clark, N. A.; Cotter, L. K.; Ackerson, B. *J. Phys. Rev. Lett.* **1986**, *57*, 1733. (d) Hurd, A. J.; Clark, N. A.; Mockler, R. C.; O'Sullivan, W. *J. Phys. Rev. A* **1982**, *26*, 2869.

[5] Monovoukas, Y.; Gast, A. P. *J. Colloid Interface Sci.* **1989**, *128*, 533–548.

[6] (a) Derjaguin, B.; Landau, L. *Acta Physicochim. URSS* **1941**, *14*, 633. (b) Verwey, E. J. W.; Overbeek, J. G. *Theory of the Stability of the Lyophobic Colloids*; Elsevier: Amsterdam, 1948.

[7] (a) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge Univ. Press: Cambridge, 1989. (b) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*; Marcel Dekker: New York, 1986.

[8] Sood, A. K. In *Solid State Physics*; Ehrenreich, H., Turnbull, D., Eds.; 1990; Vol. 43, p 1.

[9] Rundquist, P. A.; Photinos, P.; Jagannathan, S.; Asher, S. A. *J. Chem. Phys.* **1989**, *91*, 4932–4941.

[10] Haacke, G.; Panzer, H. P.; Magliocco, L. G.; Asher, S. A. U.S. Patent 5,266,238, 1993.

0002-7863/94/1516-4997$04.50/0

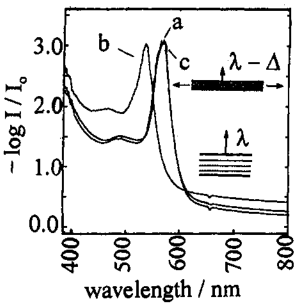

Figure 2. (a) Extinction spectra of a polymerized crystalline colloidal array (PCCA) composed of 170-nm colloidal particles polymerized in a hydrogel composed of 50% *N*-vinylpyrrolidone, 6% acrylamide, and 1% *N,N'*-methylenebis(acrylamide). The PCCA shows a diffraction maximum at 573 nm. (b) Extinction spectrum of the PCCA during a uniaxial strain in the plane of the film; the diffraction maximum shifts down to 538 nm due to the decrease in the interplanar distances. (c) Extinction spectrum of the PCCA after the stress was relieved. The PCCA again shows a diffraction maximum at 573 nm.

The water medium in the film can be replaced by other materials without changing the CCA ordering. For example, in our work[11] on developing optical limiters we have used benzyl alcohol to refractive index match a PCCA made from poly(methyl methacrylate) spheres and hydrogel network above. Although the periodic order is maintained, the refractive index matched system does not Bragg diffract light. However, any perturbation which alters the relative refractive index between the spheres and the medium causes the array to diffract light; the device becomes an optical limiter.

The liquid medium of the PCCA can also be replaced by a polymerizable monomer or inorganic glass precursor. Polymerization or condensation of this system results in a rigid film which contains the submicron periodic structure. The shape remains identical to that of the original PCCA film.

The work here demonstrates a motif for preparing solid submicron periodic systems out of a variety of materials. The only requirement is that the spherical particles must be monodisperse and possess numerous surface ionizing groups. Monodisperse spheres can be prepared from both organic and inorganic materials. Emulsion polymerization can be used to synthesize monodisperse polymer spheres from polystyrene, poly(methylmethacrylate), fluorinated polymer materials, etc.[12] Monodisperse inorganic materials can be synthesized using techniques such as the Stöber process[13] and microemulsion synthesis.[14] Electrostatic self-assembly creates a CCA periodic array with a wide variety of possible lattice constants from colloidal particles with a wide variety of particle diameters.

These systems will have numerous applications in technology. For example, they will be useful as optical filters[2a] and optical limiters[11a,b] and variable mechanically controlled wavelength rejection filters.[10]

Acknowledgment. We gratefully acknowledge support for this work from Contract F33615-88-C-5432 from Wright Patterson Air Force Base, from the University of Pittsburgh, Materials Research Center, through Air Force Contract AFOSR-91-0441, and from Air Force Grant F49620-93-1-0008 to S.A.A. We thank Dr. Hans Panzer and Lino Maggliocco for helping in some of the early studies relevant to the work described here.

Supplementary Material Available: Experimental details for polymerizing the array (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(11) (a) Asher, S. A.; Kesavamoorthy, R.; Jagannathan, S.; Rundquist, P. *SPIE Vol. 1626 Nonlinear Optics III*; 1992; pp 238–241. (b) Kesavamoorthy, R.; Super, M. S.; Asher, S. A. *J. Appl. Phys.* **1992**, *71*, 1116–1123.

(12) Matijevic, E. *Langmuir* **1986**, *2*, 12.

(13) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1963**, *26*, 62.

(14) Chang, S.-Y.; Liu, L.; Asher, S. A. *J. Am. Chem. Soc.*, submitted.