

Facile Conversion of Colloidal Crystals to Ordered Porous Polymer Nets

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We have discovered a completely new way of making an ordered porous net material with uniform pore size through a simple one step solvent vapor treatment of a colloidal crystal of an amphiphilic copolymer. The nets have potential as photonic band gap materials, membranes, and catalyst supports. Similar holey materials have been prepared from colloidal crystals by filling the void spaces with sol–gel precursors to metal oxides, fine colloidal metal oxides, polymerizable monomers, colloidal metals, or colloidal semiconductors, solidifying the material in the voids and then removing the parent spheres by chemical erosion or calcination.^{1–9} However, solvent vapor treatment is much easier than any previous procedure.

Emulsion copolymerization of a hydrophilic with a hydrophobic monomer, such as 2-hydroxyethyl methacrylate (HEMA) with styrene, leads to latexes with a core–shell structure. Due to the amphiphilic nature of the copolymer, one can selectively solvate one component to achieve structure modifications. We synthesized monodisperse latexes of styrene with 5–10% HEMA as described by Cardoso et al.^{10,11} and produced colloidal crystalline layers on glass by vertical evaporative deposition.¹² The particles have a raspberry-like texture with a polyHEMA rich shell and polystyrene rich core.^{10,11} Bands of colloidal crystals of areas up to 3 cm² formed over 2 days at 25 °C from a 0.5% solids dispersion with a stream of air passing through the headspace of the growth chamber. The crystalline bands were highly iridescent, appearing green, blue, purple, or pink, depending on the viewing angle. The scanning electron microscopic (SEM) images in Figure 1A and 1B show *fcc* colloidal crystals with the hexagonal (111) planes parallel to the substrate, as reported for polystyrene spheres.^{7,11} Although other SEM images show that the films contain small numbers of cracks, line defects, and holes, the crystals are oriented in the same direction over an area of 3 × 1 cm².

To prepare an ordered polymer net sample, either styrene or toluene was placed in the bottom of a glass jar, a glass slide coated

with the colloidal crystalline film was placed in the jar 10 mm above the solvent, and the jar was sealed for 3 h or more at room temperature. During the solvent vapor treatment, the opaque colloidal crystalline film gradually became transparent. After drying in air at room temperature, the film remained transparent and slightly iridescent. Contact with liquid solvent completely destroyed the order of the sample. The SEM images of the vapor-treated sample, Figure 1C–E, show a polymer net having holes at the same periodicity on the surface as the spheres in the colloidal crystal and cross sections of holes with hexagonal and square order. The film of the net covers the same area as the original colloidal crystal. The larger cracks remain in the surface, and smaller ones, such as line defects, close. The cross-sectional images show a modest compression of the film in the vertical direction.

We attribute the dramatic change of morphology of the films during exposure to styrene or toluene to a structural rearrangement of the polymer that originates from the core–shell structure of the latex. Emulsion copolymerization of HEMA and styrene consumes mostly HEMA early in the process.¹³ Then continued polymerization of styrene gives particles having cores rich in polystyrene and shells rich in hydrated polyHEMA. This model is supported by interfacial elemental concentration measurements using X-ray photoelectron spectroscopy (XPS) and by high-resolution SEM using a field emission gun in either the back-scattered or the secondary electron imaging modes.^{14,15} Upon exposure to vapors of a good solvent for polystyrene and poor solvent for polyHEMA, the solvent permeates into the cores of the particles, swells the polystyrene-rich phase, and lowers its glass transition temperature from 100 °C to subambient. To minimize surface energy, the now mobile polystyrene-rich phase migrates to the air-polymer interface and engulfs the minor HEMA-rich phase. As solvent evaporates, the swollen polymer shrinks, and holes appear where the cores of the spheres were before. The center-to-center distance between the holes in the net shown in Figure 1C is the same as that between the particles in the colloidal crystal.

The conversion of spheres with a polyHEMA-rich surface to a net with a polystyrene-rich surface is supported by both XPS and wetting measurements of the films. Advancing and receding contact angles of 85 ± 2° and 90 ± 2° for the colloidal crystal and 140 ± 3° and 109 ± 3° for the net respectively were measured by the dynamic Wilhelmy plate method.¹⁶ The large contact angle hysteresis of the net may be attributed to its rough surface.¹⁷ Thus, the colloidal crystal is wettable with water, and the net is more hydrophobic. XPS spectra show a much higher oxygen content from polyHEMA at the surface of the colloidal crystal than from the surface of the net. Surface rearrangements of films of HEMA/styrene block copolymers forming solid-phase structures with much smaller domain sizes also have been observed after alternating exposures to water and air.^{18,19}

The Bragg diffraction of visible or near-infrared light is vital for the application of colloidal crystalline materials and ordered

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- Holland, B. T.; Blanford, C.; Stein, A. *Science* **1998**, *281*, 538.
- Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802.
- Zakhidov, A. A.; Baughman, R. H.; Iqbal, Z.; Cui, C.; Khayrullin, I.; Dantas, O.; Marti, J.; Ralchenko, V. G. *Science* **1998**, *282*, 897.
- Jiang, P.; Cizeron, J.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 7957.
- Velev, O. D.; Tessier, P. M.; Lenhoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548.
- Vlasov, Y. A.; Yao, N.; Norris, D. J. *Adv. Mater.* **1999**, *11*, 165.
- Rogach, A.; Susha, A.; Caruso, F.; Sukhorukov, G.; Kornowski, A.; Kershaw, S.; Mohwald, H.; Eychmuller, A.; Weller, H. *Adv. Mater.* **2000**, *12*, 333.
- Jiang, P.; Hwang, K. S.; Mittleman, D. M.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 11630.
- Park, S. H.; Xia, Y. *Adv. Mater.* **1998**, *10*, 1045.
- Cardoso, A. H.; Leite, C. A. P.; Galembeck, F. *Langmuir* **1998**, *14*, 3187.
- Cardoso, A. H.; Leite, C. A. P.; Zaniquelli, M. E. D.; Galembeck, F. *Colloids Surf. A* **1998**, *144*, 207.
- Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132.

(13) Kamei, S.; Okubo, M.; Matsumoto, T. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 3109.

(14) Cardoso, A. H.; Leite, C. A. P.; Galembeck, F. *Langmuir* **1999**, *15*, 4447.

(15) Okubo, M.; Yamamoto, Y.; Kamei, S. *Colloid Polym. Sci.* **1989**, *267*, 861.

(16) Teeters, D.; Wilson, J. F.; Andersen, M. A.; Thomas, D. C. *J. Colloid Interface Sci.* **1988**, *126*, 641.

(17) Adamson, A. W. *Physical Chemistry of Surfaces*, 3rd ed.; John Wiley & Sons: New York, 1976; pp 345–347.

(18) Lewis, K. B.; Ratner, B. D. *J. Colloid Interface Sci.* **1993**, *159*, 77.

(19) Senshu, K.; Yamashita, S.; Ito, M.; Hirao, A.; Nakahama, S. *Langmuir* **1995**, *11*, 2293.

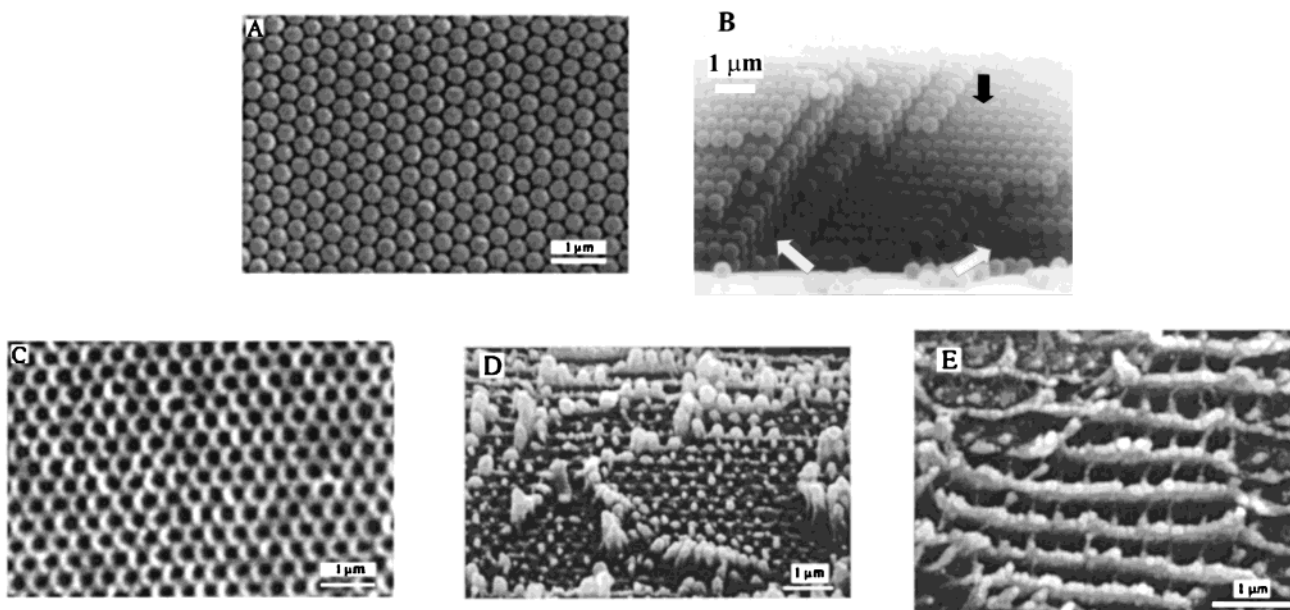


Figure 1. (A) SEM image of the top surface of colloidal crystals of poly(HEMA-co-styrene) spheres 369 ± 13 nm in diameter coated with gold/palladium. (B) Surface exposed by fracture of a different film of the same particles. The internal (111) hexagonal facet (vertical arrow) forms a 109.5° angle with the top hexagonal surface, and the (100) square facets (tilted arrows) form a 54.7° or 125.3° angle with both hexagonal planes, which indicates fcc packing. This sample is 17 spheres, or $5 \mu\text{m}$, thick. (C, D, E) SEM images after treatment of a colloidal crystalline film with styrene vapor. The top surface (C) has a hexagonal arrangement of holes with center-to-center distance ≈ 370 nm. The cross section (D) shows a porous network with holes arranged hexagonally, and cross section (E) has holes arranged tetragonally. The projecting stubs of polymer in (D, E) are due to distortion of the net during fracture.

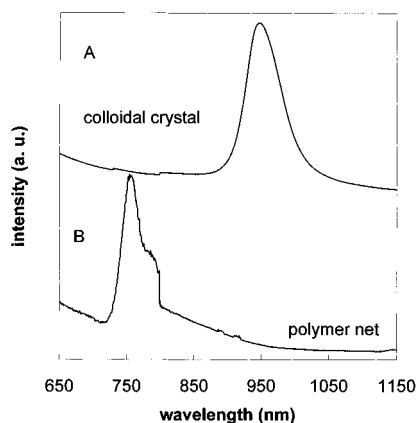


Figure 2. Visible-NIR transmission spectra of (A) a colloidal crystalline film and (B) a polymer net film. The transmission minima are at 944 and 752 nm, and the bandwidths at half-height are 58 and 36 nm, respectively. Extinction at the minimum is 85 times greater for A than for B. There is a spectrophotometer artifact at 800 nm.

nets as optical filters^{20,21} and switches^{22,23} and for their potential as photonic band gap materials.²⁴ Figure 2 shows transmission spectra of light normal to the surface of the colloid crystal and the net samples. The colloidal crystal has a strong band with

minimum transmittance in the NIR at 944 nm, while the net has a much weaker band shifted toward the visible at 752 nm. The decrease in extinction of the net is due at least in part to a decrease in long-range order, and a different form factor for scattering by the net and varied local gradients of refractive index of the polymer may also contribute. The shift of the band to shorter wavelength is attributed qualitatively to partial collapse in the direction normal to the film plane as the net is formed, which is apparent in Figure 1D.

This new method for transformation of colloidal crystalline films of polymer spheres into ordered porous polymer nets should be applicable to a wide range of copolymer latexes whose components have substantial differences in solubilities.

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- (20) Carlson, R. J.; Asher, S. A. *Appl. Spectrosc.* **1984**, *38*, 297.
 (21) Sunkara, H. B.; Jethmalani, J. M.; Ford, W. T. *Chem. Mater.* **1994**, *6*, 362.
 (22) Kesavamoorthy, R.; Super, M. S.; Asher, S. A. *J. Appl. Phys.* **1992**, *71*, 1116.
 (23) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. *Science* **1996**, *274*, 959.
 (24) Joannopoulos, J. D.; Meade, R. D.; Winn, J. N. *Photonic Crystals: Molding the Flow of Light*; Princeton University Press: Princeton, NJ, 1995.