

Fabrication of Three-Dimensional Macroporous Membranes with Assemblies of Microspheres as Templates

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Although a number of methods are available for producing macroporous materials with pore sizes ≥ 50 nm,¹ it still remains a great challenge to fabricate macroporous membranes that have precisely controlled pore sizes, well-defined surfaces, and three-dimensionally interconnected porous structures. Traditional methods based on electrochemical etching of alumina or silicon,² chemical etching of glasses,³ and ion-track etching of polymers⁴ are only capable of generating macroporous membranes with one-dimensional channel structures. Methods based on foaming of emulsion solutions⁵ and sintering of ceramic particles⁶ have very little control over the distribution of pore size. Methods based on assembly of block copolymers⁷ can only form spherical pores that are isolated from each other. Recent demonstrations based on replication against various kinds of templates^{8–11} provide a simple and effective route to three-dimensional macroporous membranes with precisely controlled pore sizes and pore structure, but these methods still have problems in completely exposing all pores on both top and bottom surfaces of the membrane films. Here we describe an improved procedure that allows formation of macroporous membranes of organic polymers or inorganic ceramics that exhibit the following features: (1) spherical pores whose dimensions can be precisely controlled in the range from ~ 0.2 to ~ 3 μm , (2) three-dimensionally interconnected networks of pores in the bulk, and (3)

completely exposed pores on both top and bottom surfaces of membrane films.

Figure 1A shows the schematic procedure that we have used.^{12,13} A cell was constructed by sandwiching a square frame of photoresist between two glass substrates. The square frame was fabricated on the bottom substrate using a two-step photolithographic procedure:¹⁴ (1) a photoresist (Microposit 1075, Shipley, MA) film was spin-coated on the bottom substrate and then exposed to UV light for ~ 67 s through a mask with a test pattern of a square frame on its surface; (2) the resist film was then exposed to UV light for an additional ~ 5 s through another mask covered with a test pattern of parallel lines (500 μm in width and separated by 100 μm). The two masks were aligned such that the parallel lines on the second mask only overlapped with one side of the square frame. As a result, an array of trenches (< 0.3 μm deep) was generated on this side of the frame after developing; these trenches subsequently served as channels for the flow of solvent.

When an aqueous dispersion of polystyrene beads (~ 0.05 wt %, Polysciences, Warrington, PA)¹⁵ was injected into the cell, a positive pressure of N_2 was applied through the glass tube to force the solvent (water) to flow through the channels. The polystyrene beads were accumulated at the bottom of the cell and assembled into a polycrystalline lattice (Figure 2A) very quickly under sonication.¹⁶ When all solvent disappeared from the cell, a liquid precursor of polyurethane (NOA-73, Norland Products, New Brunswick, NJ) was introduced into the cell and then solidified by exposure to UV light.^{17,18} Because the polystyrene beads were confined by the walls of the cell, the assembled lattice of the polystyrene beads was essentially unchanged in this process: the liquid prepolymer only filled the void spaces among the polymer beads. When the two substrates were carefully separated, a free-standing thin film (Figure 2B) of a composite of cross-linked polyurethane and polystyrene beads was obtained. Subsequent dissolution (Figure 1B) of the polystyrene beads in toluene (for ~ 10 min) produced a membrane of polyurethane that has a three-dimensional network of

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(14) The thickness (H) of the cell is approximately the same as the thickness of the photoresist film, which can be easily changed from ~ 0.5 to ~ 50 μm by using different photoresists, different concentrations of solutions, and/or different speeds for spin-coating. The photoresist films used in the present study were ~ 12 μm thick.

(15) A variety of monodispersed microspheres, including polystyrene beads, silica colloids, silver-coated polystyrene beads, and polycarbonate beads, have been successfully assembled using this procedure (see refs 12 and 13), and their sizes can vary from ~ 0.1 to 10 μm . Here we have only used 0.97- μm polystyrene beads to demonstrate the capability of the procedure.

(16) The rate of packing along the direction of solvent flow increased as the pressure of N_2 gas increased. When the packing is too fast, polycrystalline rather than single crystalline assemblies are formed. Since polycrystalline assemblies are still useful in fabricating thin film membranes, we used a rate of ~ 3 mm/h (for a 12- μm -thick and 2-cm-wide cell) for generating all the assemblies of 0.97- μm polystyrene beads used in fabricating the membranes.

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(18) We can also fabricate three-dimensional macroporous membranes of inorganic ceramics (e.g., SiO_2 and TiO_2) by injecting appropriate sol-gel precursors instead of organic prepolymers. See refs 10 and 11.

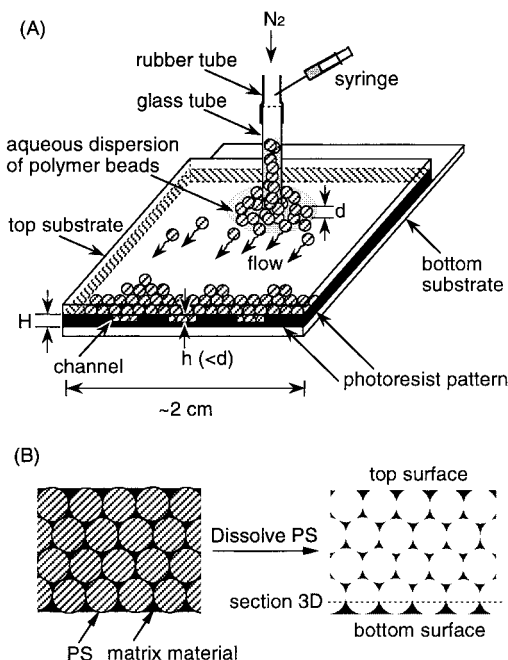


Figure 1. (A) A schematic outline of the procedure for producing crystalline assemblies of polystyrene beads. The aqueous dispersion of polystyrene beads is injected into the cell through the rubber tube using a syringe. The diameter (d) of particles that can be directly assembled in the cell is determined by the depth (h) of the channels; d must be larger than h . (B) Formation of a three-dimensional macroporous membrane by dissolving the template of assembled polystyrene beads in toluene.

spherical pores in the bulk; all the pores are interconnected to each other through tiny "windows" and are completely exposed on both top and bottom surfaces. The membrane floating on the surface of toluene was transferred onto a frame (made from a copper wire) by picking up the membrane with the frame from underneath.¹⁹

Figure 3 shows SEM images of a polyurethane membrane (supported on a glass substrate) that was fabricated from a polycrystalline lattice of 0.97- μm polystyrene beads. The pores on the top surface of the membrane are $\sim 0.5 \mu\text{m}$ in diameter; the density of these pores on the surface is $\sim 10^8/\text{cm}^2$. The bulk porosity of this kind of membrane is approximately 74%, a value that is determined by close packing.²⁰ The spherical pores in the bulk film are interconnected to each other by circular "windows" that are $\sim 0.3 \mu\text{m}$ in diameter (as indicated by an arrow in the bottom SEM of Figure 3). On the basis of the ideal model of cubic-close-packing, each spherical pore should be connected to six other pores in the same plane and three other pores above and below the plane. In our case, each pore is expected to be connected to less than 12 adjacent pores, since a polycrystalline lattice was used as the template. Unfortunately, we were unable to reveal the exact structure of this three-dimensional macroporous membrane without using confocal optical microscopy.

(19) The largest free-standing membrane that we have been able to fabricate using this procedure is $\sim 1 \text{ cm}^2$ in area; this result clearly demonstrates the structural integrity of the polymer membrane.

(20) The porosity should be greater than 74% if we consider the "windows" that connected the spherical pores into the three-dimensional network.

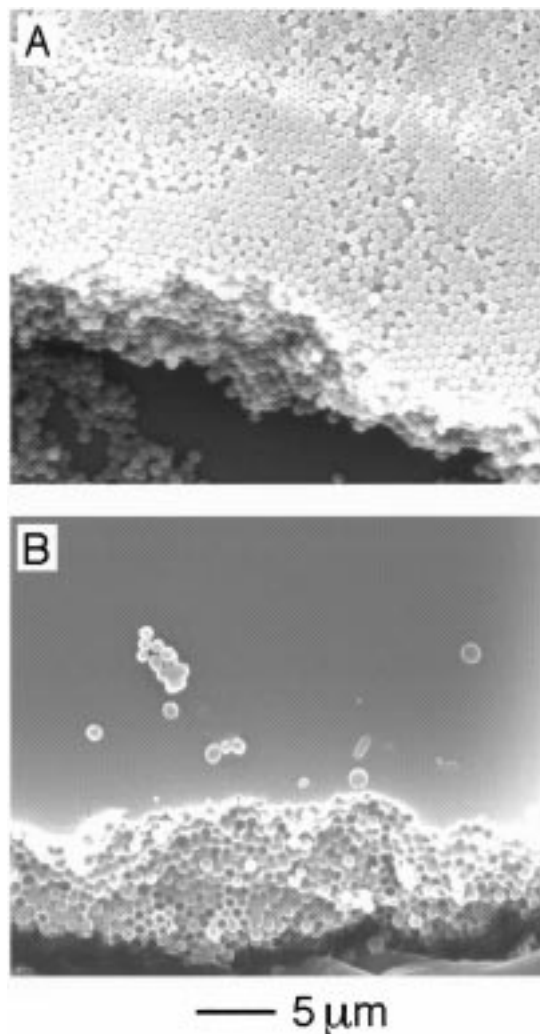


Figure 2. (A) The cross sectional SEM image of a polycrystalline lattice assembled from 0.97- μm polystyrene beads in a 12- μm -thick cell. (B) The cross sectional SEM image of a free-standing film of a composite of polystyrene beads and cured polyurethane.

Figure 4A shows the SEM of a portion of another polyurethane membrane that was fabricated by replication against a crystalline lattice of 0.97- μm polystyrene beads. This membrane has been broken to reveal the three-dimensional architecture of the spherical pores in the bulk of the film. Figure 4B shows the SEM of a portion of the broken membrane that simultaneously displays the top surface (Figure 4C), the bottom surface (Figure 4D, that is, the section 4D as indicated in Figure 1B), and the cross section of the membrane. As indicated in Figure 1B, it is reasonable that the pores on the top and bottom surfaces may appear to be isolated from each other and that the diameter of the pores on the section 3D is larger than the that of the pores on the top or bottom surface.

In summary, we have demonstrated a convenient and versatile method for producing complex and truly three-dimensional membranes that have precisely controlled pore sizes and completely exposed pores on both top and bottom surfaces. This procedure can be applied to a variety of materials including organic polymers and inorganic ceramics; the only requirement seems to be the availability of a liquid precursor that does not swell or dissolve the template. Although this procedure may

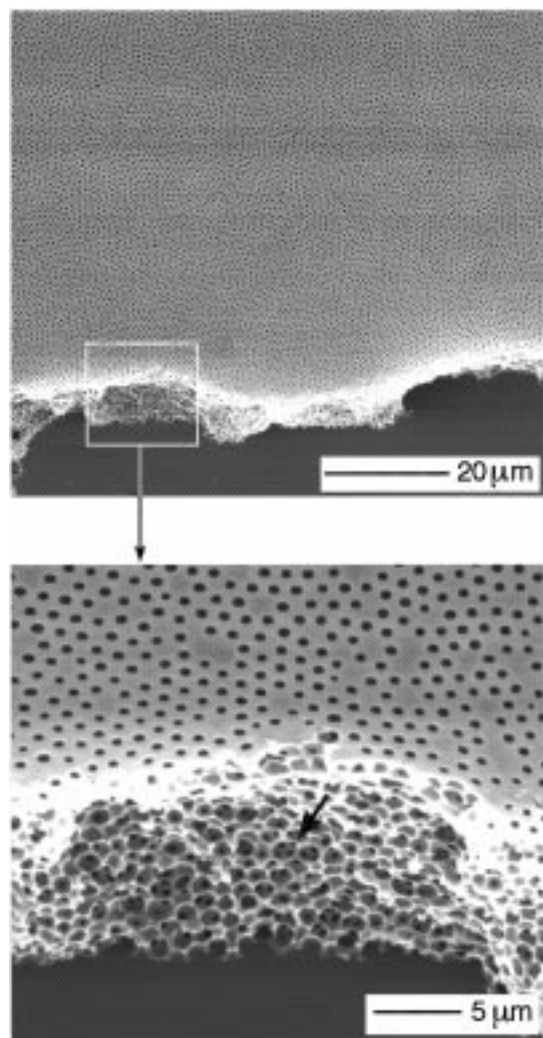


Figure 3. Cross sectional SEMs of a polyurethane membrane that was fabricated by using a polycrystalline lattice of 0.97- μm polystyrene beads as template. In this three-dimensional macroporous membrane, each spherical cage is connected to adjacent cages through very small "windows" (indicated by an arrow).

lack the characteristics required for mass production, it can efficiently produce membranes with precisely controlled pore sizes and well-defined (both surface and bulk) porous structures that can be used as model systems to study a number of interesting subjects, such as adsorption, condensation, transport (diffusion and flow), and separation of molecules in macroporous materials, as well as mechanical and optical properties of three-dimensional porous materials.²¹ The three-

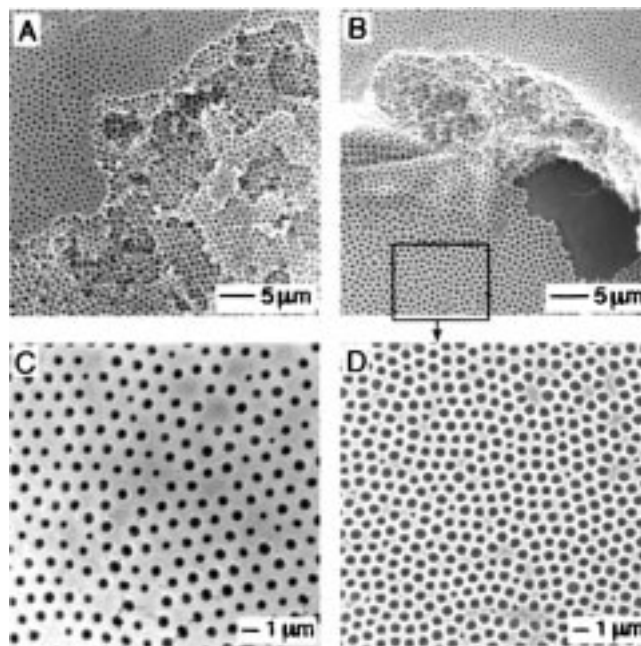


Figure 4. (A, B) SEMs of a polyurethane membrane that has been broken to reveal the three-dimensional network of pores inside the film. The membrane was fabricated by replicating against a template of 0.97- μm polystyrene beads. (C) An SEM of the top surface of the membrane. (D) An SEM of the bottom surface (that is, the section 3D in Figure 1B) of the membrane.

dimensional open structures fabricated using this procedure can also be used as substrates (with appropriate surface modifications) to fabricate prototype sensors with enhanced sensitivities²² or as templates to generate three-dimensional complex structures of various functional materials that cannot be fabricated using conventional photolithographic techniques.²³

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