



Euromembrane Conference 2012

[P2.186]

Gold coated block copolymer membranes with precisely controllable pore size for molecule separations

H.Z. Yu*, X.Y. Qiu, K.V. Peinemann

King Abdullah University of Science and Technology, Saudi Arabia

The need to physically separate similarly sized solutes is a ubiquitous problem in biological research and in the production of biomolecules and other nanoparticles. Compared to resin-based chromatography, membrane separations are simpler, more energy efficient, and more readily scaled between laboratory and industry. To create idealized membranes for size-based separations, researchers have developed nanoporous membranes with well-defined and tunable pore sizes. Aluminum oxide and track-etched membranes are commercially available examples, but the pores in these membranes are too large (>20nm) for many biological separations.¹ Silicon patterning techniques have been used to create membranes with uniform 10 nm wide pores, but the low porosity (~1%) of these membranes limit the transport.² Ultrathin silicon membranes (~10 nm) with defined pores (25 nm) were first created using an ion-beam drilling process that is far too slow for up-scaling.³ Recently, track-etching technology has been applied to SiN membranes to create 100 nm thick membranes with pore sizes that can be tuned between 10 nm and 50 nm depending on the time allotted to etching; however, this technique faces high volume manufacturing challenges.⁴

On the other hand, self-assembly has been considered as one of the most important methods to achieve nanostructures or nano-objects with well-defined shapes, sizes, and long-range order. For materials scientists, block copolymers are a material of choice for achieving nanostructures based on micro phase separation. Self-assembly of amphiphilic block copolymers has attracted a lot of scientific interest over the past decade. Amphiphilic block copolymers can self-assemble into well-defined supramolecular structures on a mesoscopic length scale between ten and several hundred nanometers. The nanometer length scale of periodic structures is difficult to achieve using other materials or techniques. When dissolved in selective solvents, amphiphilic block copolymers may self-assemble into spherical or cylindrical micelles, vesicles and other structures. An especially attractive application of block-copolymer self-assembly is the formation of isoporous membranes. A major problem in this process is the lack of sufficient long-range order, precisely controllable pore size and the difficulty of up-scaling due to the time-consuming preparation steps.⁵

Here, an innovative and simple method was utilized to fabricate an integral asymmetric membrane by combining the self-assembly of amphiphilic block copolymer of polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) and non-solvent-induced phase separation. The preparation process of asymmetric films consisted of the following steps: (1) casting of a 200- μ m-thick film on a glass plate with a doctor blade, (2) solvent evaporation at room temperature for typically 10 s, (3) immersion in a non-solvent bath (water) at room temperature, and (4) drying at ambient conditions. The resulting films showed a non-transparent white color and had an average thickness of 90 μ m. The polymer-rich phase (PS blocks) forms the porous matrix, whereas the polymer-poor phase (P4VP blocks) gives rise to the pores. The structure comprises a top thin layer (~100 nm) exhibiting highly ordered cylindrical pores with uniform size perpendicular to the surface at extremely high density and a non-ordered sponge-like layer beneath (Figure 1). This asymmetric morphology is a direct consequence of the combination of two different processes, the conventional non-solvent-induced phase separation and the self-assembly of block copolymers. The diameter of the vertically aligned cylinders at the membrane surface is approximately 35

nm. The effective pore diameter is smaller, because the pores are lined with P4VP. This very fast one-step manufacture of membrane can be easily up-scaled.

The free pair of electrons in the nitrogen of P4VP can be used for the formation of metallized nanostructures. It may capture metal ions such as Au^{3+} . The nitrogen-metal complexes in metal nanostructures could serve as nucleation sites to produce stable coatings around the nanostructures. Therefore, the P4VP blocks inside the nanopores have the potential to be excellent templates for metallic nanostructures formation to control the pore size. By wet electroless plating routes under a wide range of conditions, the hydrophilic blocks (P4VP) may selectively form a complex with metal ions. The Au nanoclusters were deposited as a result of a direct redox reaction on the walls of the nanopores. Therefore, the pore diameter of the nanoporous membranes could be well controlled through such a simple wet electroless plating methods. To fabricate the Au layer on the surface of the pore walls, the membranes were first immersed in a solution of Au^{3+} . Afterwards the membranes were rinsed several times with distilled water to remove excess Au^{3+} on the surface of the membrane. Then, Au^{3+} was reduced by treating with reduction solution. The thickness of the Au layer can be varied by varying the plating time or the concentration of Au^{3+} . We can clearly see that the pore diameter decreased after Au deposition (Figure 1b). Figure 2 shows scanning electron microscopy (SEM) images for the top surface of the nanoporous membranes after Au deposition. Cylindrical pores with different diameters were uniformly formed in the nanoporous membrane, as shown in Figure 2. The pore size decreased with increasing the thickness of the Au deposition layer on the membrane. After deposition of the Au layer on the surface of the membrane, the pore diameter can be reduced from 34.2 nm to 14.5 nm, and 9.2 nm, as calculated based on SEM images. It is worth to note that the effective pore diameter is smaller as estimated from water flow experiment using Hagen-Poiseuille equation. This membrane formation method integrates a classical process of phase separation and a simple electroless deposition process and is up-scalable for industrial membrane casting equipment. To examine the performance of the block copolymer membranes after Au deposition in size-exclusion separations, we are performing separation experiments on a protein size ladder containing several proteins with different size and molecular weight. Given the hours-long passage-times of molecules through thick membranes, the proteins will be forced to through the membrane in a centrifuge which can enhance the separation efficiency.

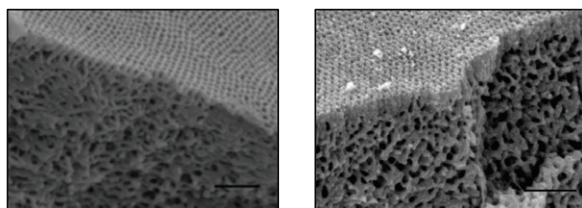


Figure 1. SEM images of the cross-section of the membranes: (a) before Au deposition, (b) after Au deposition. The scale bars represent 500 nm.

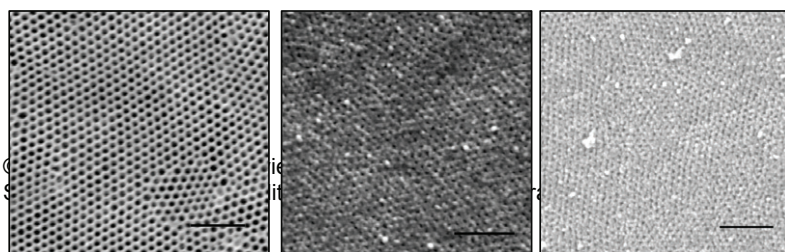


Figure 2. SEM images of membranes with different pore diameter after gold deposition: (a) 34.2 nm, (b) 14.5 nm, (c) 9.2 nm. The size was calculated based on SEM images. The scale bars represent 500 nm.

Reference

- (1) Martin, C. R.; Siwy, Z. Molecular Filters: Pores within Pores. *Nat. Mater.* 2004, 3, 284-295.
- (2) Fissell, W. H.; Dubnisheva, A.; Eldridge, A. N.; Fleischman, A. J.; Zydney, A. L.; Roy, S. High-Performance Silicon Nanopore Hemofiltration Membranes. *J. Membr. Sci.* 2009, 326, 58-63.
- (3) Tong, H.; Jansen, H.; Gadgil, V.; Bostan, C.; Bereschot, E.; van Rijin, C.; Elwenspoek, M. Silicon Nitride Nanosieve Membrane. *Nano Lett.* 2004, 4, 283-287.
- (4) Vlassiuk, I.; Apel, P. Y.; Dmitriev, S. N.; Healy, K.; Siwy, Z. S. Versatile Ultrathin Nanoporous Silicon Nitride Membranes. *Proc. Natl. Acad. Sci. U.S.A.* 2009, 106, 21039-21044.
- (5) Peinemann, K.V.; Abetz, V.; Simon, P. F. W. Asymmetric Superstructure formed in a Block Copolymer via Phase Separation. *Nat. Mater.* 2007, 6, 992-996.