

Supporting Information

Accompanying “Composite Block Polymer-Microfabricated Silicon Nanoporous Membrane”

by E. E. Nuxoll, M. A. Hillmyer R. Wang, C. Leighton & R. A. Siegel

Fabrication details for silicon support

A 100 μm thick double-side-polished $\langle 100 \rangle$ silicon wafer (University Wafer, Boston) is coated with 40 nm of low stress silicon nitride (Si_3N_4) by low pressure chemical vapor deposition (99 sccm SiH_2Cl_2 , 20 sccm NH_3 , 305 mTorr, 843 $^\circ\text{C}$). The bottom side is spin-coated with Shipley 1813 photoresist at 3000 rpm for 30 s to protect it from subsequent etching steps. After soft-baking for 90 s at 105 $^\circ\text{C}$, the top side of the wafer is spin-coated, first with hexamethyldisilazane (adhesion promoter), and then Shipley 1818 photoresist, each at 1000 rpm for 30 s. After softbaking for 90 s at 105 $^\circ\text{C}$, the wafer is exposed to g-line (436 nm) UV light for 12 s through a darkfield mask containing up to 52 50 x 50 arrays of 20 μm squares spaced 20 μm apart. After 60 s developing in diluted (20%) Microposit 351 developer the wafer is rinsed, dried and mounted atop a 500 μm thick handle wafer using spin-coated photoresist dots to glue the edges of each wafer together. This wafer stack is then hard-baked at 120 $^\circ\text{C}$ for 150 s and subjected to 60 s of reactive ion etching (RIE, 40 sccm CF_4 , 4 sccm O_2 , 100 mTorr pressure, 100 W power) to remove the exposed top-side Si_3N_4 squares. Bosch-process directed reactive ion etching (DRIE) anisotropically etches these squares through the silicon wafer. Bosch-process DRIE etching was carried out at ~ 22 mTorr and ambient temperature via helium cooling in 3-step cycles w/ 825 W RF power. Deposition step gases were 40 sccm Ar, 0.5 sccm SF_6 and 70 sccm C_4F_8 . Those rates changed to 40, 50, 0.5, respectively for the first etch step and 40, 100, 0.5 for the second. Cycles averaged 17 s duration with relative durations of 5:2:6. A typical etch time was 50 min. Variation in etch rate and wafer thickness (up to 15%) can result in wafer over- or underetching. Over-etching results in thinning of the 40 nm Si_3N_4 pore covering at a rate of about 20 nm/min as well as lateral etching of the Si at the Si/ Si_3N_4 interface. Underetched devices require an additional DRIE step. The etched wafer is removed from its handle and is cleaned by oxygen RIE (99 sccm O_2 , 100 mTorr, 100 W) for 15 minutes on each side.

Additional fabrication details

Block copolymer solution was 30 mg/mL in chlorobenzene, spin-coated onto the support at 4000 rpm for 30 s. Low power RIE for removing residual polymer from the bottom of the nanopores was performed with 80 sccm O₂, 30 mTorr pressure and 60 W power.

Pattern Transfer from block polymer to nitride

A low stress silicon nitride film was spin coated with block polymer, then subjected to RIE etching according to the following recipe:

Gas Flow Rates: Argon – 50 sccm \pm 5%, CHF₃ – 50 sccm \pm 5%, CF₄ – 25 sccm \pm 5%.

Power: 150 W \pm 5%

Chamber Pressure: 75 mTorr \pm 5%

Etch duration: 2.5 – 4.0 min, according to polymer thickness and desired nitride pattern depth.

UV/Vis calibration/detection limit

0.0457 g methyl orange was dissolved in 500 ml water. 1500 μ L of this solution constituted sample O1. Another 300 μ L was dissolved in 900 μ L water, constituting sample O2. 300 μ L of O2 was dissolved in 900 μ L of water to form O3, which in turn was used to make samples O4, O5 and O6 in via subsequent 1:3 dilutions.

Similarly, 0.4833 g dextran blue was dissolved in 4.9614 g water at ambient temperature and 150 μ L of this solution was added to 1350 μ L water to form reference sample B1. Sequential 1:3 dilutions with water were used to make samples B2 through B6. Each sample was scanned for UV absorption.

Figure S1 below plots methyl orange absorbance at 464 nm vs. concentration. The absorbance for sample O1 is above 2, in an unreliable range for measuring absorbance. The remaining samples fall on a straight line ($R^2=0.999989$) indicating

$$\text{Absorbance}(464\text{nm}) = 71.83 \times \text{Concentration}(\text{mg/mL}) - 0.0111.$$

The presence of an intercept (substantiated by an absorbance of -0.0048 against the reference cell for the most dilute sample) indicates a measurement bias which calls into question observations at extremely low absorbance. While replicate measurements at low concentration indicated variation only a fraction of the intercept magnitude, readings below 0.022 mg/mL (twice the negative intercept) were not trusted as reliable indicators of methyl orange concentration. Similarly, Figure S2 plots dextran blue absorbance at 618 nm vs. concentration. Sample B1, with an absorbance above 2, is neglected and the remaining data fall on a straight line ($R^2=0.999998$) indicating

$$\text{Absorbance}(618\text{nm}) = 0.7387 \times \text{Concentration}(\text{mg/mL}) - 0.0161.$$

Again, readings below 0.0322 (twice the negative intercept) were not trusted as reliable indicators of dextran blue concentration. This corresponds to minimum methyl orange and dextran blue concentrations of 0.00031 mg/mL and 0.043 mg/mL, respectively. The transport trials were designed to permit measurements at concentrations above these limits. Methyl orange had no detectable absorption at 618 nm, even at high (0.1 mg/mL) concentration. The extinction coefficient of dextran blue at 464 nm is about 10% that at 618 nm, though it was never present at sufficient downstream concentration to make this absorption relevant.

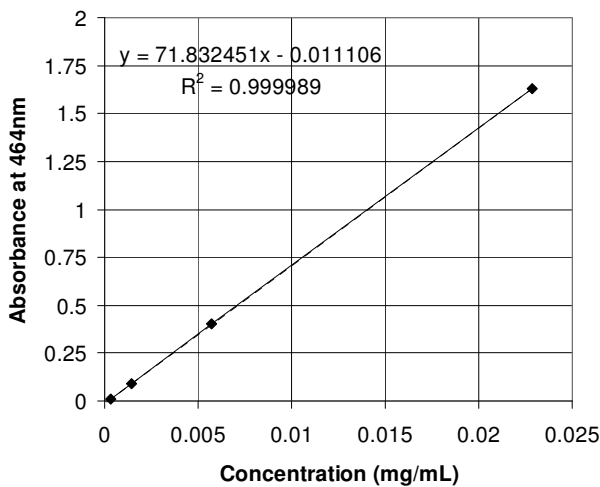


Figure S1: Methyl Orange UV/Vis Calibration

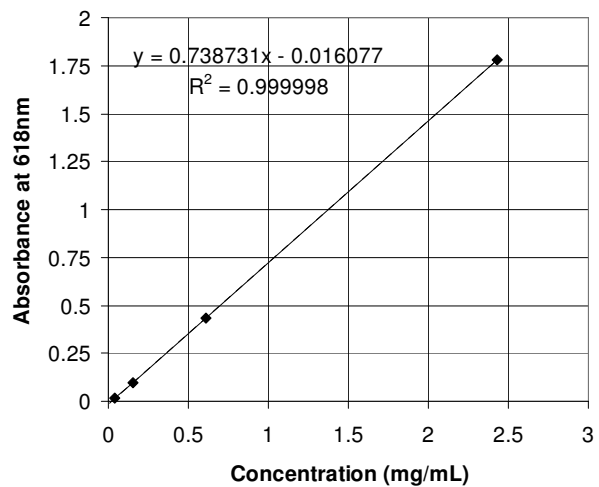


Figure S2: Dextran Blue UV/Vis Calibration

Diaphragm Cell Experiments

To evaluate transport resistance and size selectivity, the bilayered composite was mounted between polyethylene washers and sandwiched between two 3 ml diffusion cells (Crown Glass). To ensure wetting of the membrane, each cell was first loaded with a milliliter of isopropyl alcohol then flushed with 155 mM saline. Vertical ports on the cells allowed the pressure head of the downstream cell to be kept a few centimeters above that of the upstream cell in order to assure that any convective flux due to potential membrane flaws would not swamp the diffusive flux measured downstream.

To investigate transport, 0.82 mL of saline in the upstream cell was replaced with the same amount of saturated methyl orange (Sigma, MW=327 g/mol) solution. The cells were then stirred and 0.5 mL samples were periodically removed from the downstream cell and replaced with saline. Two hours later, after confirming mass transport through the membrane, stirring was stopped while 0.7 mL of upstream solution was replaced by the same volume of 97 mg/mL dextran blue (Sigma, MW=2,000 kg/mol) solution. Stirring resumed and the downstream cell was periodically sampled. Samples were diluted 1:1 with saline and analyzed by UV/Vis spectroscopy. To minimize the effect of sampling on solute accumulation, after the first week 0.7 mL samples were removed, immediately assayed, and returned to the downstream cell. Saline was occasionally added to the downstream cell to make up for evaporative loss. The upstream cell, which had a narrow 3 cm port between the liquid level and the environment, showed only slight volume loss.

As a control, a similar trial was performed using a commercial anodized alumina membrane (Anodisc, Whatman) with nominal pore size 200 nm to offer much less size exclusion. In this trial, dextran blue was introduced immediately after methyl orange, and pressure heads were kept within 1 mm of each other to minimize convective transport. As this membrane had much larger (~16X) surface area, flux was much higher and sampling was much more frequent. Where the trial with the composite membrane took six weeks, the control trial with Anodisc lasted two days and was performed twice, concurrent to the composite membrane trial.

In another control, a composite membrane was prepared without removing its PLA. In its transport trial, no methyl orange was observed downstream for the first 18 hours, after which a 0.5 mL downstream sample was replaced with the same volume of 0.37M NaOH. Five and a half hours later, with methyl orange clearly diffusing downstream, 1.05 mL of upstream solution was replaced with 150 mg/mL dextran blue solution. Samples from the downstream cell were assayed and returned three and five days after introduction of the dextran blue.

Estimate of Fluid Boundary Layer in Diaphragm cell experiments

The simplest estimate of the fluid boundary layer in a diaphragm cell experiment uses the slope of the solute breakthrough curve (e.g. Figure 9) to determine the solute flux across the membrane. For example, the MO solute breakthrough curve for Control 2 is roughly linear for the first 90 minutes with a slope of 0.253 ng/mL/min (knowing that C_o for that case was 0.259 mg/mL). Knowing that the downstream volume was 2.88 mL, the flux appears to be 0.729 ng/min. The concentration gradient decays by nearly 18% during this time, with an average value of 0.233 mg/mL. Assuming a porosity of 50% for the 9 mm diameter Anodisc membrane, the area available for diffusion is 0.318 cm². The diffusion coefficient of methyl orange in water is about 1.2×10^{-5} cm²/s. Plugging these numbers into Equation S1,

$$J = \frac{(D)(A)(\Delta C)}{\ell} \quad (\text{S1})$$

where J is the solute flux, D is the diffusion coefficient, A is the membrane area, ΔC is the solute gradient and ℓ is the diffusion pathlength, we find ℓ to be around 730 μm . This corresponds to a 60 μm membrane with a 335 μm boundary layer on each side.

A more careful approach accounts for the significant amount of MO lost from the downstream cell during each sampling period. Here, the total amount of solute crossing the membrane between samples is determined by concentration difference between samples plus the amount of solute removed during the earlier sampling. Since this is calculated after each sample, the flux during that interval can

be used as J with the corresponding ΔC during that interval to determine an ℓ for that interval. Using this method, the average ℓ value was around 520 μm , corresponding to a boundary layer of 230 μm . Similar calculations were done on each trial, some with boundary layers less than 100 μm , complicating any direct comparison of flux among different membranes in different cells.

Instrumentation

RIE etching was performed on an STS Model 320 reactive ion etcher. DRIE etching was performed on a Plasmatherm SLR770 etcher. AFM images were taken on a Digital Instruments Nanoscope III Multimode. SEM image was taken on a JEOL 6700 Field Emission Gun Scanning Electron Microscope. Confocal microscopy images were taken on a Hyphenated Systems HS200A optical microscope. UV/Vis measurements were obtained with a Cary 100 spectrophotometer in disposable PS cuvetts.