Pore Size Control of Ultra-thin Silicon Membranes by Rapid Thermal Carbonization

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Supporting Information

Pore distribution analysis and electron microscopy

Pnc-Si has the distinct advantage over other porous membranes of being amenable to characterization by transmission electron microscopy due to its small thickness ~ 15 nm. As such, pore distributions can be directly calculated from TEM micrographs using custom MATLAB scripts (available for download at nanomembranes.org/resources/software), see figure S-1. Details can be found in Gaborski *et al*.[1] Typically, an 11 um x 17 um micrograph is used to calculate the distribution.

Plan-view transmission electron microscopy of pnc-Si membranes was performed in bright-field mode at 80 keV using a Hitachi H-7650 Transmission Electron Microscope (Tokyo, Japan). Test membrane samples were integrated on each wafer to be compatible with the TEM specimen holder. Images were acquired with an Olympus Cantega 11 megapixel digital camera.

Pnc-Si structure is stable at high temperatures

To verify that the pore structure is only affected when acetylene is present, a control sample was annealed at 800°C for five minutes in argon only[2]. Electron microscopy and pore histogram analysis shows that the mean diameter was unchanged after annealing (Figure S-2) leading us to conclude that pnc-Si membranes are unaffected by a thermal treatment in argon alone.

Carbonization rate versus pore size

We have found that the rate of carbonization is not dependent on the starting pore size as demonstrated in figure S-3. A membrane was carbonized for 10 minutes at 750°C in 10% acetylene (WARNING: acetylene is extremely reactive when in contact with oxygen

and other oxidizers. Do not pressurize more than 15 psig or 103 kPa). The width of the carbon along the pore walls was measured directly from a TEM micrograph in Photoshop. The carbon deposit width of 21 pores representative of the entire size distribution were measured using TEM and found to have a standard deviation of 3.4 Å.

Chemical stability of carbonized pnc-Si membranes

Carbonized and untreated samples were soaked in %5 (w/v) KOH (Mallinckrodt Baker, Phillipsburg, NJ) at 40°C for one hour in an oven. The samples were rinsed with distilled and deionized water and dried. Pnc-Si membrane chips normally appear purple when the SiO_2/pnc-Si film stack is intact. It was clear from the silver color of the bare silicon chip that the untreated membrane had completely dissolved while the carbonized membrane remained intact (S-4).

Ozone treatment of pnc-Si membranes

In order to ensure wetting of all the pores in a pnc-Si membrane, we have ozone treated all the samples prior to permeability and separation experiments (Novascan PSD-UVT, Ames, IA). Ultra-high purity oxygen (Airgas, Rochester, NY) was allowed to flow through an ozone generator and introduced into the specimen chamber. The membranes are heated to 150°C and a mercury vapor lamp is used to remove organic contaminants from the surface as well as generate ozone. A 10-minute treatment of carbonized membranes did remove a small amount of carbon coating (Figure S-5). Ozone treatment of carbonized membranes increased the hydrophilicity of the surface as evidenced by the contact angles formed by water droplets on the membrane surface (Figure 1).

Hydraulic permeability of carbonized pnc-Si membranes

Custom polypropylene vials that housed ultrathin silicon membranes were used in water permeability experiments (SiMPore, Inc., West Henrietta, NY). A polydimethylsiloxane (PDMS) Sylgard® 182 elastomer was used to seal the membrane chip to the plastic insert (Dow Corning, Midland, MI). The plastic vial assembly was then loaded into a custom aluminum pressure cell. 500 uL of DI water was placed inside the vial and the assembly was sealed with a Viton® gasket. 40 uL of water was placed on the bottom membrane surface (i.e. filtrate side) to initiate wetting of the pores. The vial was pressurized to 3.0 PSI (read using a manometer) for five minutes. Water was collected with an eppendorf tube and the hydraulic permeability was calculated using the expression[1]:

$$\varepsilon = \frac{V}{P \cdot A \cdot t} \qquad \text{(Equation S-1)}$$

where ε is the hydraulic permeability, V is the total volume passed (minus the initial 40 uL used for wetting), P is the pressure applied, A is the membrane active area, and t is the elapsed time.

The Dagan equation[3] for fluid flow through a short pipe was used to predict the permeability of our membranes:

$$Q = \frac{r^3 \Delta P}{\mu\left[3 + \frac{8}{\pi} \cdot \frac{l}{r}\right]} \qquad \text{(Equation S-2)}$$

where Q is the volumetric flow rate, r is the pore radius, P is the pressure drop across the pore, μ is the solution viscosity, and l is the length of the pore. A custom MATLAB script was written to calculate the theoretical permeability using a pore distribution acquired from TEM micrographs[1]. An example of this analysis is shown in figure S-6.

Gold nanoparticle filtration

Stock solutions (0.01% w/v) of gold nanoparticles (British BioCell International, Cardiff, UK) were diluted 1:1 with DI H_2O. 200 uL of diluted gold was placed in assembled plastic inserts with pnc-Si membranes and pressurized to 3 PSI using the pressure cell described above. Pressure was maintained until approximately one-half of the volume passed through the membranes (typically 5-15 minutes). The retentate and filtrate solutions were recovered and weighed to determine total volume recovery, which was typically 150 uL. The retentate solution was pipetted up and down against the membrane five times to maximize recovery of gold that had settled against the membrane. The peak absorbance between 500-550 nm of the retentate and filtrate was measured using a Tecan plate reader (Tecan Group, Männedorf, Switzerland) and compared to stock solution peak values, see figure S-7. A "blank" scan was taken with distilled water and used to adjust the filtrate readings to account for any discrepancies in absorbance of the plate. Using the volume and concentrations of the retentate and filtrate, percent nanoparticle passage was calculated.

Protein filtration

Cytochrome c, bovine serum albumin (BSA), and β-galactosidase were purchased from Sigma (St. Louis, MO) and reconstituted in 1x phosphate buffered saline (PBS) at a concentration of 1 mg/mL (w/v). Solutions were spun at 10,000g for 5 minutes to sediment any aggregates or non-dissolved material. The supernatant was recovered and used for the following separation experiments. Concentrations were calculated from fits to standard curves of absorbance at 280 nm (BSA and β-galactosidase) and 410 nm

(cytochrome c). The limit of detection was approximately <0.05 mg/mL. The sieving coefficient (C/C_0) was calculated similarly to the nanoparticle separation experiments.

Experiments were performed by first placing 200 uL of protein solution in the plastic membrane insert. The bottom side of the membrane was briefly wetted with 1x PBS to initiate flow and then drawn off with a pippeter[1]. The device was pressurized to 3 PSI and experiments were allowed to run until at least 50 uL of filtrate solution could be collected (typically 30 min to 1 hr). The filtrate solution was then measured using the Tecan absorbance scanner. The raw absorbance scans and standard curves are shown in figure S-8. A "blank" scan was taken with 1x PBS and used to adjust the filtrate readings to account for any discrepancies in absorbance of the quartz plate.

Figures

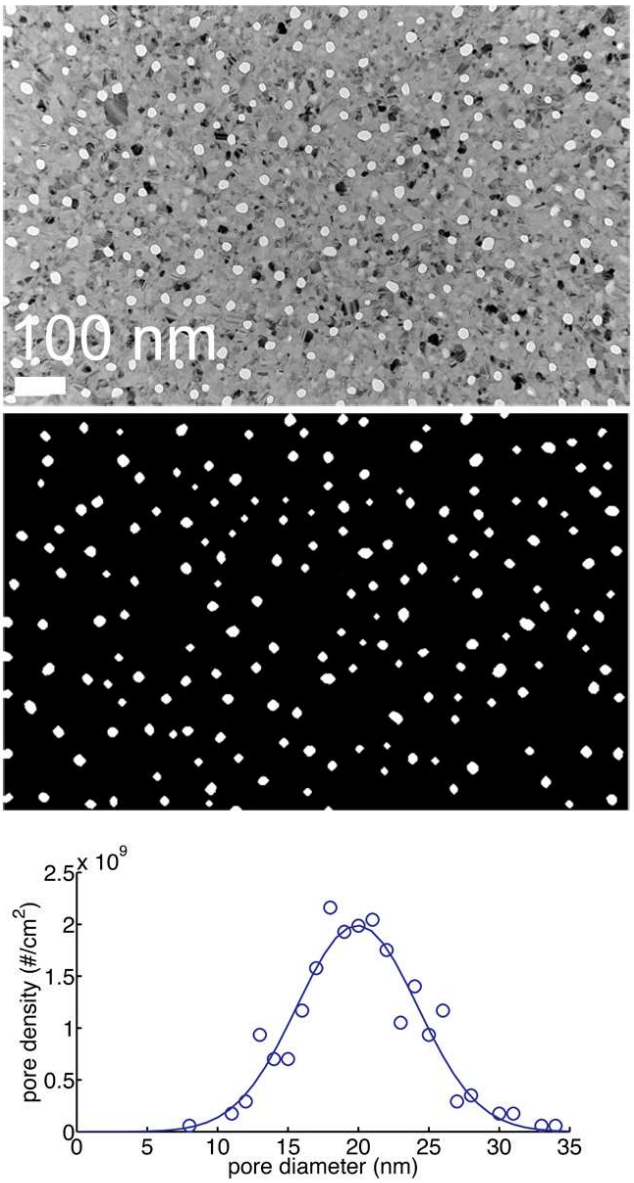

Figure S-1. Pore size distribution calculation using custom MATLAB scripts for pore recognition. A TEM micrograph is processed into a binary image, where pore sizes can then be calculated and size distributions generated. The open blue circles represent measured densities at a specific diameter and the solid line is a normal fit.

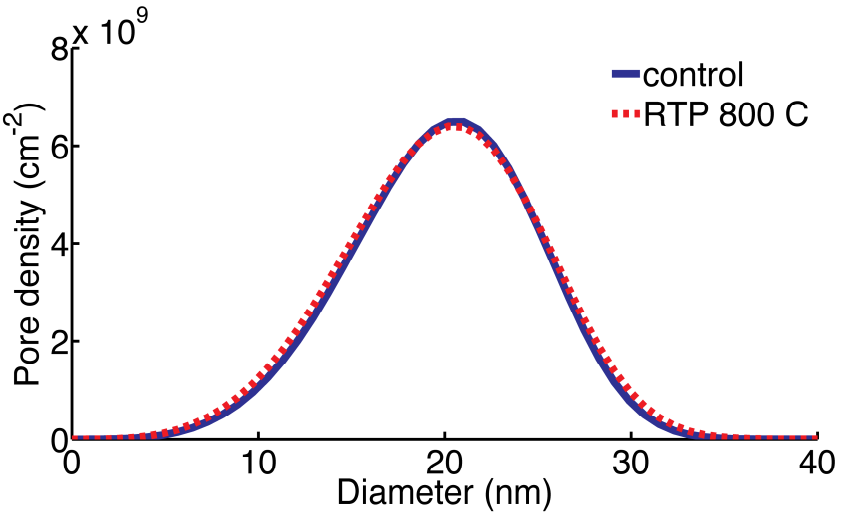

Figure S-2. Pore distribution of a membrane annealed for five minutes at 800°C in 10 slm of Ar. There is no change in pore structure before and after annealing.

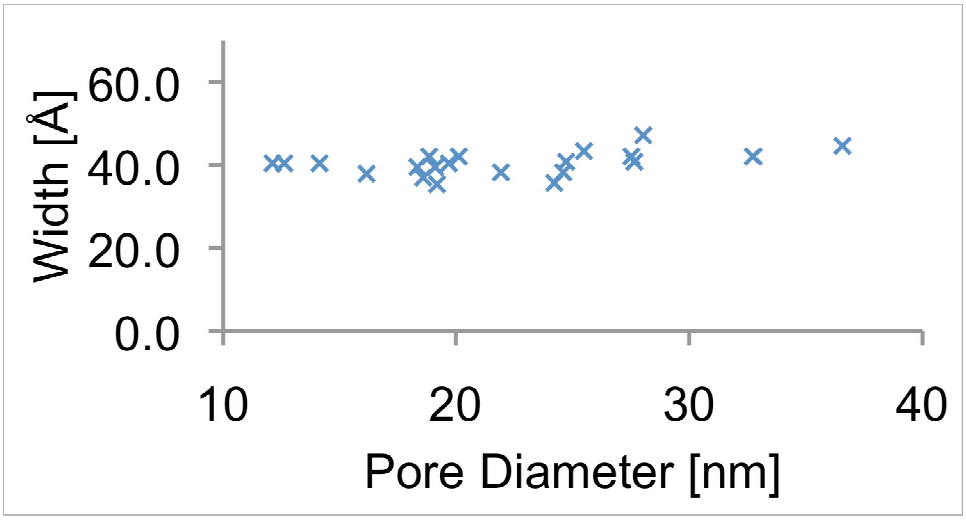

Figure S-3. Width of carbon deposit width versus pore size. The growth rate of carbon is unaffected by pore size.

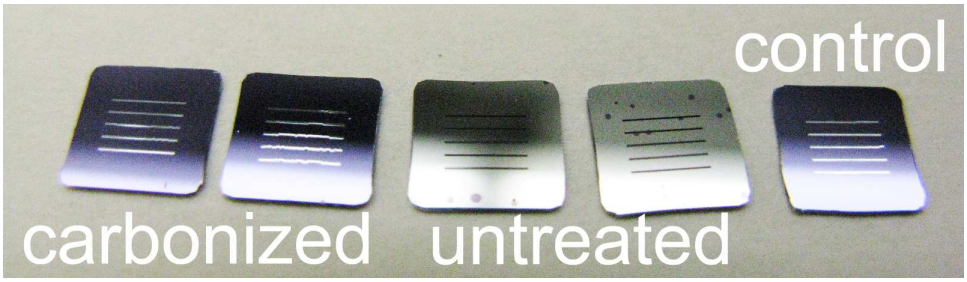

Figure S-4. Carbonized and untreated pnc-Si membranes after 1 hour in %5 KOH at 40°C. The rectangular slits are free-standing pnc-Si. Untreated membranes are discolored indicating the dissolution of the silicon film[3].

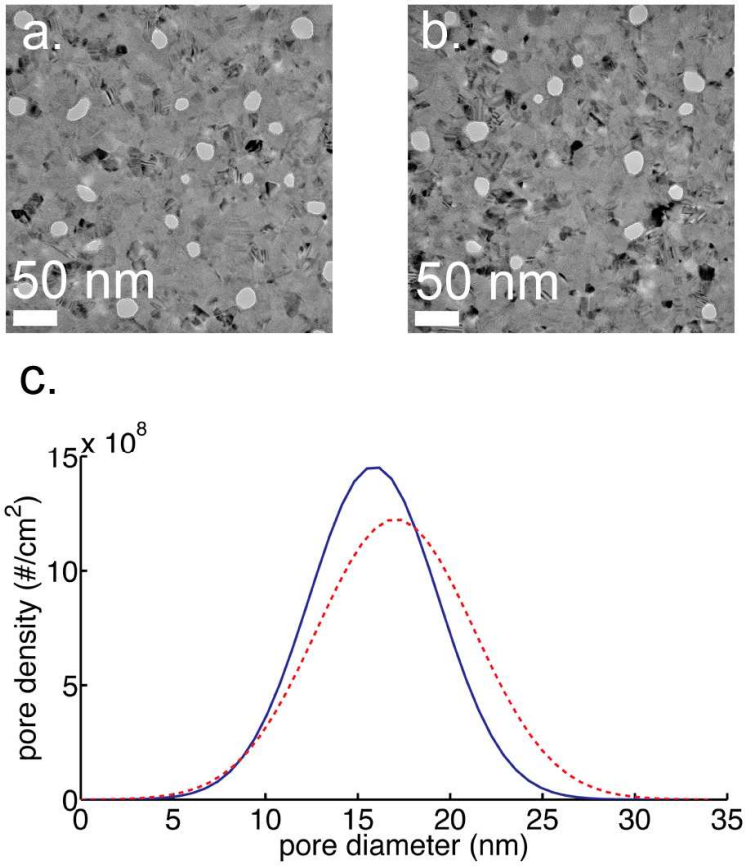

Figure S-5. Bright-field TEM micrograph of (a) carbonized membrane and (b) carbonized/ozone treated membrane. (c) Pore size distribution before (blue solid) and after (red dashed) ozone treatment. The pores are slightly enlarged after treatment.

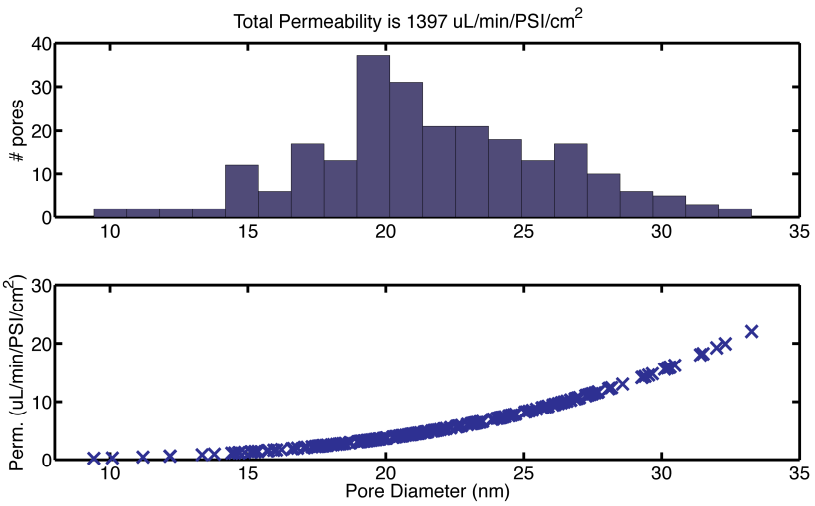

Figure S-6. Calculation of the theoretical hydraulic permeability from the size distribution of an actual membrane using the Dagan equation on a pore-by-pore basis.

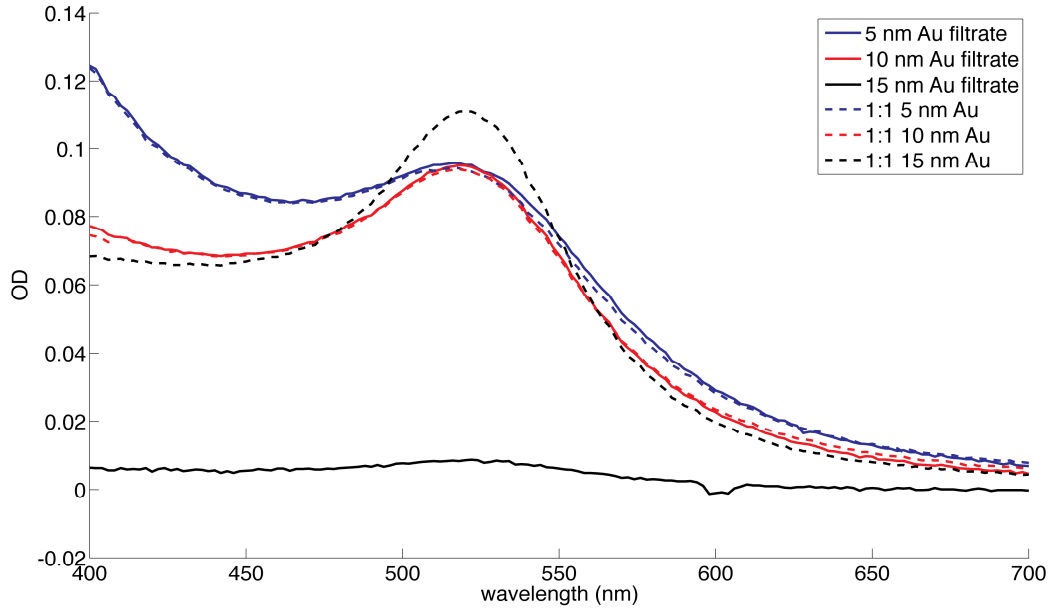

Figure S-7. Sample absorbance scan of several filtrate solutions and the 1:1 gold colloid dilutions.

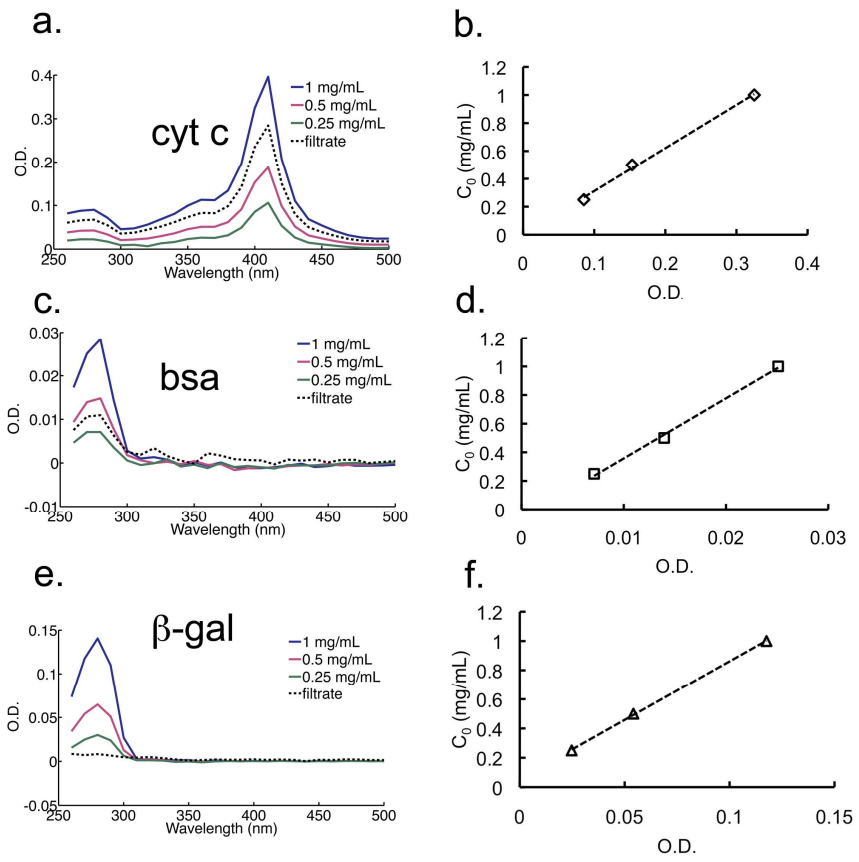

Figure S-8. Raw absorbance data and standard curves. The standard curves were generated by taking the absorbance peak at 280 nm for BSA and β-galactosidase and 410 nm for cytochrome c.

References

1. Gaborski, T. R.; Snyder, J. L.; Striemer, C. C.; Fang, D. Z.; Hoffman, M.; Fauchet, P. M.; McGrath, J. L. *ACS Nano* **2010**, In Review.
2. Agrawal, A. A.; Nehilla, B. J.; Reisig, K. V.; Gaborski, T. R.; Fang, D. Z.; Striemer, C. C.; Fauchet, P. M.; McGrath, J. L. *Biomaterials* **2010,** 31, (20), 5408-5417.
3. Dagan, Z.; Weinbaum, S.; Pfeffer, R. *J. Fluidic Mech. Digital Archive* **1982,** 115, (1), 505-523.