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Fabrication of a Carbon Nanotube-Embedded Silicon Nitride Membrane for Studies of Nanometer-Scale Mass Transport

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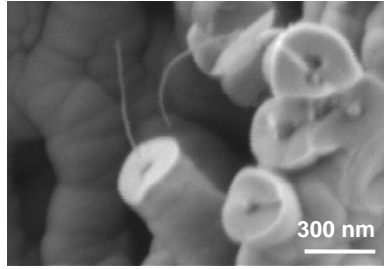
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ABSTRACT

A membrane consisting of multiwall carbon nanotubes embedded in a silicon nitride matrix was fabricated for fluid mechanics studies on the nanometer scale. Characterization by tracer diffusion and scanning electron microscopy suggests that the membrane is free of large voids. An upper limit to the diffusive flux of D₂O of 2.4×10^{-8} mole/m²-s was determined, indicating extremely slow transport. By contrast, hydrodynamic calculations of water flow across a nanotube membrane of similar specifications predict a much higher molar flux of 1.91 mole/m²-s, suggesting that the nanotubes produced possess a “bamboo” morphology. The carbon nanotube membranes were used to make nanoporous silicon nitride membranes, fabricated by sacrificial removal of the carbon. Nitrogen flow measurements on these structures give a membrane permeance of 4.7×10^{-4} mole/m²-s-Pa at a pore density of 4×10^{10} cm⁻². Using a Knudsen diffusion model, the average pore size of this membrane is estimated to be 66 nm, which agrees well with TEM observations of the multiwall carbon nanotube outer diameter. These membranes are a robust platform for the study of confined molecular transport, with applications in separations and chemical sensing.

A number of recent studies¹⁻⁵ have focused on the development of membranes with nanometer-scale pores. Such membranes could find application in the area of size-based chemical and biological separations, provided pore sizes can be reduced to molecular diameters and a high flux of the permeate molecule can be achieved. On this size scale, however, little is known about the behavior of fluids; deviations from continuum transport can occur as the channel size becomes comparable to molecular diameters. For example, it is known that the intra-pore diffusivity (as compared with the bulk diffusivity) decreases when the pore size becomes comparable to molecular dimensions.⁶ In electrolyte solutions, if the pore radius is comparable to the Debye length (electrical double layer thickness), a situation can arise where the ion concentration within the pore exceeds that of the bulk solution,⁷ which may have some interesting consequences for the development of ion-selective membranes.

An ideal system for the study of confined molecular transport is a carbon nanotube, which has an inner diameter as small as 1 nm. Not surprisingly, a number of recent molecular dynamics simulations have focused on transport within these materials.⁸⁻¹⁰ Many exotic predictions have been made, from the formation of novel phases of ice⁸ and pulsed one-dimensional water transport,⁹ to the spontaneous insertion of ss-DNA into a single wall carbon nanotube.¹⁰ What has been lacking, however, is a platform for experimentally verifying some of these predictions.

One method explored involves chemical vapor deposition of carbon within the pores of an alumina membrane.² Typically, the pore sizes achieved by this approach (of order 100 nm) are larger than the size range of interest for chemical and biological separations. In addition, the inner walls of these carbon nanotubules are only semigraphitic and thus do not possess the inherent smoothness of a purely graphitic carbon nanotube (CNT). It is also reported² that tubes prepared in this manner possess acidic surface sites (-COOH) on their walls. The inherent smoothness and inertness of a purely graphitic CNT are the attributes that molecular dynamics simulations¹¹ predict give rise to a high molecular flux through CNTs.

Another method for preparation of such a membrane involves embedding an amorphous carbon coated graphitic tube in an epoxy matrix.¹ However, the resultant pore diameter in these materials is again large (~150 nm). A method that has managed to produce membranes in the single nanometer size regime involves creating damage tracks in a polycarbonate film by use of a collimated fission fragment beam, followed by etching in basic solution.³ With subsequent electroless plating, single gold nanotubes of order 2 nm were prepared. More recently, a polystyrene-coated CNT membrane was fabricated.⁵ The pore sizes of this membrane are reported to be consistent with that of multiwall CNT inner diameters (~ 7.5 nm).

The method described in this study involves producing a CNT-based membrane using low-stress silicon nitride as a conformal matrix material. To the author's knowledge, this research constitutes the first attempt at producing a truly graphitic CNT membrane using a ceramic matrix material. In contrast to polymer matrices, silicon nitride has a negligible molecular permeability, leaving the cores of embedded CNTs as the only pores in the membrane. Alternatively, these nanotubes can serve as a template for the production of nanoporous silicon nitride by selectively removing them via oxidation. The other advantage offered by silicon nitride is its vapor phase deposition. Polymers spun-on to CNT arrays require elaborate curing processes⁵ to reduce CNT agglomeration and ensure retention of alignment.

The entire fabrication process for these membranes is illustrated in Fig. 1. Our starting material is single-side polished test grade Si(100). The catalyst used for nanotube growth is iron, deposited by electron beam evaporation to a thickness between 2.5-5.0 nm. The samples are annealed shortly after the deposition of iron (500°C, 1 hour, 10 sccm O₂) to oxidize the surface, a common practice.¹² We have observed that samples which undergo room temperature oxidation in air over several days have a reduced catalytic efficiency, producing a lower density array of nanotubes. Samples are next placed into an atmospheric pressure CVD system (1" diameter tube furnace) and initially exposed to a reducing

environment of Ar/H₂ (600 sccm/400 sccm) as the temperature is ramped up to the growth temperature of 850°C for a period of 20 minutes. At this point, discrete iron nanoparticles form, with diameters in the range from 20-100 nm. The diameter distribution is skewed towards smaller particles as the iron thickness is decreased. These nanoparticles serve as the catalyst and nucleation sites for nanotube growth. After temperature stabilization, C₂H₄ (1000 sccm) is introduced to initiate growth. Nanotube growth occurs for 20 minutes and results in a dense array of multiwall nanotubes of ~ 5-10 μm length and 20-50 nm diameter, as shown in Fig. 2a; tube areal densities are typically 4x10¹⁰ cm⁻². The crucial step in our process is filling the voids between the nanotubes with a rigid, impermeable material that conforms to them, to enable further processing into a membrane. Low-stress silicon nitride possesses these desirable properties. After tube growth, the samples are placed into a low pressure CVD furnace to deposit a low-stress silicon nitride layer, using a deposition temperature of 800°C and a 6:1 ratio of dichlorosilane to ammonia. A target film thickness between 400-800 nm was found sufficient to fill the bulk of the 5-10 μm thick nanotube forest and encapsulate the top. Due to the non-oxidizing atmosphere for the silicon nitride process, carbon nanotube damage is not observed at these elevated temperatures and the tubes retain their alignment through the process. Also, there is little concern over the filling of the nanotube interior with silicon nitride, as we have observed by transmission electron microscopy (TEM) that the nanotubes grow with a graphitic cap at the top. The excellent coverage offered by this material can be seen in the image of Fig. 2b, where the film (partially fractured by preparation of the cross section) is seen to encapsulate an individual nanotube.

A number of additional processing steps are required before continuous, open channels can be formed. Reactive ion etching (RIE), using a 3.6:1 ratio of CF₄:O₂ at 150 W power, is used to open a window in the silicon nitride layer to expose the backside of the silicon substrate. This is followed by anisotropic KOH etching of the exposed silicon to uncover the nanotube/silicon nitride film. To remove excess silicon nitride deposited atop the CNTs (opposite the silicon substrate), as well as open their tips,

RIE is used once again. Alternatively, Ar-ion milling can be used under conditions of 0.5 kV ion energy and 1 mA/cm² beam current density; due to the lack of chemical selectivity, this process typically produces a much smoother surface. It is important that this tube-opening step occurs after the KOH wet processing to avoid the possibility that the exposed carbon nanotubes are filled by liquids. Examination of the interface where the silicon was removed by KOH etching (referred to as the “backside” of the membrane) reveals a number of bright particles (Fig. 2c), which were confirmed by Energy Dispersive X-ray (EDX) analysis to contain iron. Consideration of their size (20-50 nm), comparable to the outer diameter of the carbon nanotubes, suggests that these are residual iron catalyst particles not removed during the prior processing steps. As many of these particles would block access to the core of the nanotube, a strategy for their removal was devised. This consists of a brief RIE process (or the aforementioned ion milling process) to remove a few nm of silicon nitride and further expose the iron nanoparticles. Fig. 2c depicts the backside of the membrane after the ion milling process, with pores of 40-90 nm evident, comparable in size to the iron nanoparticles and the nanotube outer diameter. After the etching/ion milling step, the iron nanoparticles are removed by immersion of the sample in concentrated HCl for 24 hours. Subsequent EDX analysis confirmed the removal of the vast majority (>90%) of the nanoparticles. At this stage, the carbon nanotube membrane fabrication is complete. If a nanoporous silicon nitride membrane is desired instead, the nanotubes can be removed by an oxidation treatment (800°C, 10 sccm O₂, 1 hour).

The mechanical integrity of these membranes is a critical issue for their subsequent characterization. Due to the inherent brittle nature of ceramic materials like silicon nitride, voids that remain after processing (due to incomplete coverage of the nanotube array) can lead to cracks and ultimately fracture the membrane; Fig. 2d is a cross-sectional image of the membrane in which such voids in the interior of the membrane are evident. However, the CNTs may provide a modest reinforcement effect, as the work of Ma *et al.*¹³ on multiwall CNT-silicon carbide composites suggests, by deflecting cracks that might otherwise propagate and rupture the membrane. To test the mechanical

integrity of the CNT-silicon nitride composites fabricated in this study, fully processed CNT membranes were mounted in an O-ring sealed fixture with one side open to air and the other placed under vacuum. Only one out of five membranes fractured under these testing conditions. Using an expression derived from van Rijn *et al.*,¹⁴ the theoretical maximum pressure drop a solid silicon nitride membrane can withstand prior to rupture is given as:

$$\Delta P = 0.29 \left(\frac{t_m}{r_m} \right) \sigma_{\text{yield}} \sqrt{\frac{\sigma_{\text{yield}}}{E}} \quad (1)$$

where t_m is the membrane thickness (5 μm), r_m is the membrane radius (2.5 mm), and σ_{yield} and E are the yield stress and Young's modulus for the silicon nitride. Using the yield stress of bulk silicon nitride of 4 GPa and a Young's modulus of 385 GPa,¹⁵ a value of approximately 2 atm is calculated for our experimental geometry. The observation that most of our CNT-membranes could withstand a comparable pressure drop (1 atm) suggests that the voids in the bulk of the material do not significantly weaken the membrane and produce cracks. The nanoporous silicon nitride membranes were observed to be similarly robust, suggesting that nanotube reinforcement may not be significant and that it is the overall low void fraction of the membrane that accounts for its strength.

Another concern during processing is whether the voids in the interior of the membrane will be uncovered during etching of the silicon nitride. Cross-sectional micrographs of these membranes have shown a continuous, void-free region extending ~ 100 nm from the silicon interface (Fig. 2d). As another gross check on membrane integrity, and to ensure that the large voids are not propagating through the membrane, fluorescent tracer experiments were conducted. Epoxy was used to bond the fully processed CNT membrane to reservoirs on either side. In one side, pure water was used, while in the opposite, fluorescently-labeled polystyrene beads of first 100 nm, then 25 nm diameter (in a separate experiment) were placed in solution, both smaller than the apparent voids of several 100 nm in Fig. 2d. After a period of 48 hours, solution from the pure water reservoir was extracted and examined by fluorescence confocal microscopy. There was no evidence for diffusion of the labeled polystyrene

beads in either experiment, suggesting that these voids in the membrane interior do not propagate through, leaving the nanotube interior as the most likely conduit for molecular transport. These measurements were followed by isotopic tracer measurements where deuterated water (D_2O) was placed in one reservoir, with pure water in the other. After a period of 24 hours, a sample was extracted from the pure water reservoir and analyzed by stable isotope mass spectrometry, with a sensitivity of approximately 1 part per million deuterium relative to hydrogen.¹⁶ There was no evidence for diffusion of D_2O in this case, which provides an upper bound on the rate of permeation through our membranes of 2.4×10^{-8} mole/ m^2 -s (as determined by the sensitivity of the analytical technique). This is in sharp contrast to the flux of 0.29 mole/ m^2 -s, calculated by molecular dynamics simulations for diffusion through considerably smaller single wall carbon nanotubes.⁹ If indeed the only open channels in this experiment consisted of the interior of the carbon nanotubes, a measurable flux of D_2O would have been expected. The low flux observed here suggests that this channel is blocked. Specifically, it is possible that the CNTs in this membrane are not hollow and instead form the well-known “bamboo” morphology,¹⁷ consisting of periodically spaced chambers along their length. In the literature, characterization of the nanotube morphology is often based on TEM of a small fraction (~100 nm) of the entire length (often in excess of 10 μ m). Thus, it seems probable that even the nominally hollow tubes reported in the literature may in fact be blocked. The CNTs in this study show evidence of the “bamboo” morphology, as can be seen in the TEM micrograph of Fig. 3.

To produce open, nanometer-scale channels through which molecular transport could be measured, a carbon nanotube membrane was placed into an oxygen furnace (800°C, 1 hour, 10 sccm O_2) to allow selective oxidation of the nanotubes. The resulting nanoporous silicon nitride membrane was then mounted in an O-ring sealed flow cell with a mass flow controller and pressure gauge upstream of the membrane. A pressurized nitrogen line was attached upstream, with the other end open to air. A control experiment utilizing a non-porous material of similar dimensions confirmed that all connections were leak tight, such that the membrane would be the only gas transport path. By measuring the flow

rate as a function of pressure drop (see Fig. 4), the permeance of the membrane could be determined. For pressure drops in the range from 50-1800 Pa (0.007-0.27 psi), a permeance of 4.7×10^{-4} mole/m²-s-Pa was determined. This compares with a value of 2.6×10^{-6} mole/m²-s-Pa, determined for a multiwall CNT membrane with pores reported to be 7.5 nm in diameter⁵, in the range expected of CNT inner diameters. Given that the membrane in this study was created by oxidative removal of the CNTs, we would expect larger pores, representative of CNT outer diameters, which in turn should lead to a larger membrane permeance. Data obtained from TEM measurements (Fig. 3) suggests a size distribution of CNT outer diameters ranging from 20-50 nm. To determine whether the measured membrane permeance can be accounted for by pores in the size range of the CNT outer diameter, we have to consider a model for molecular transport.

The behavior of fluids on the size scale of these membrane pores is expected to differ from that of bulk, continuum transport. In particular, a comparison of the mean free path at 1 atm for nitrogen (66 nm) with that of the nitride pore size (20-50 nm) suggests a transitional flow regime, between slip and free-molecule flow.¹⁸ Previous work by Itaya *et al.*¹⁹ with alumina membranes has shown that Knudsen diffusion can adequately characterize molecular transport down to 10 nm length scales. Thus, assuming Knudsen diffusion, where gas-solid collisions are treated as elastic and result in diffuse scattering, the gas molar flux across the membrane is linear in pressure drop:

$$J = \left(\frac{\pi r^2 \rho C}{V_g \sqrt{2\pi MRT}} \right) \Delta P \quad (2)$$

where r is the pore radius, M is the molecular weight, R is the gas constant, T is temperature, ρ is the pore areal density, V_g is the gas molar volume, ΔP is the pressure drop, and C is an aspect ratio dependent factor $\approx (1+0.46 \cdot L/r)^{-1}$,²⁰ with L being the effective diffusion length. Using the experimentally measured permeance \mathcal{P} ($= J/\Delta P$) of the nanoporous silicon nitride membrane, along with other membrane parameters, in the limit $L \gg r$, the average pore radius can be determined as follows:

$$r = \left(\frac{1.1\sqrt{MT} \mathcal{P} L}{\rho} \right)^{1/3} \quad (3)$$

For a typical membrane pore density of $4 \times 10^{10} \text{cm}^{-2}$ and an effective diffusion length of $10 \mu\text{m}$ (accounting for the membrane thickness and nanotube tortuosity), an average pore diameter of 66nm is determined. This value is slightly larger, but comparable to the outer diameter of CNTs observed by TEM. This larger-than-expected value could be accounted for by tightly bundled CNTs that could not be filled by the silicon nitride. For reference, the permeance of a microporous alumina filter (Whatman Anodisc) of 200nm nominal pore diameter ($60 \mu\text{m}$ thickness, $1.6 \times 10^9 \text{cm}^{-2}$ pore density) was measured, and the Knudsen diameter calculated from this measurement was $\sim 180 \text{nm}$, similar to SEM observations of the pore size. For considerably smaller pores (in the 1nm range of single wall nanotubes), it is expected that the molecule-pore interaction will differ from the simple elastic collision model assumed in Knudsen diffusion. In particular, we expect to see a dependence on the molecular coverage of the surface. Modeling and experiments in this size regime will be the subject of future studies.

Also of interest for subsequent liquid experiments is an estimate of the flux of water across a *nanotube* membrane. The method of van Rijn *et al.*²¹ was used for this calculation, which assumes viscous, laminar flow and includes correction factors for frictional losses with the walls, interference effects of neighboring pores, and neglects any nonviscous kinetic losses. Under these assumptions, in the limit $L \gg r$, the water molar flux is given as:

$$J = \left(\frac{0.12r^2}{\mu L V_w} \right) \Delta P \quad (4)$$

where μ is the liquid viscosity, V_w is the molar volume of water, and all other variables are defined as before. For a 10nm inner diameter nanotube of $10 \mu\text{m}$ length and a pressure drop of 1atm , a water flux of $1.91 \text{mole/m}^2\text{-s}$ is calculated. For a 1nm inner diameter nanotube, the corresponding water flux is $0.019 \text{mole/m}^2\text{-s}$, an order of magnitude less than the $0.29 \text{mole/m}^2\text{-s}$ value determined for a similar size

single wall nanotube, using molecular dynamics-based transport rates.⁹ However, it is unclear whether the assumption of no-slip along the walls, used in the hydrodynamic model, is satisfied for the smooth, hydrophobic interior of a carbon nanotube,²² and this alone may account for the discrepancy in these two values. This is a topic under active investigation.

In summary, a robust, void-free membrane that can be used for the study of nanofluidics has been developed by standard microfabrication techniques, consisting of multiwall carbon nanotubes embedded in a silicon nitride matrix. A nanoporous silicon nitride membrane was formed by the oxidative removal of these carbon nanotubes from the silicon nitride matrix. The gas permeability of this nanoporous silicon nitride membrane was confirmed and the nitrogen permeance determined. Assuming Knudsen-type diffusion through the membrane, an average pore size of 66 nm is calculated, which is comparable to that of the multiwall nanotube outer diameter. The calculated rate of water transport (in the hydrodynamic limit) of 1.91 mole/m²-s through a smaller pore nanotube membrane suggests that the structure would be suitable for liquid-based experiments and potential nanofluidic devices. Future studies are geared towards controlling deposition parameters to suppress the formation of “bamboo” CNTs, as well as fabrication of an analogous single wall nanotube membrane, which should bring us closer to verifying some of the exotic molecular transport properties predicted for CNTs.

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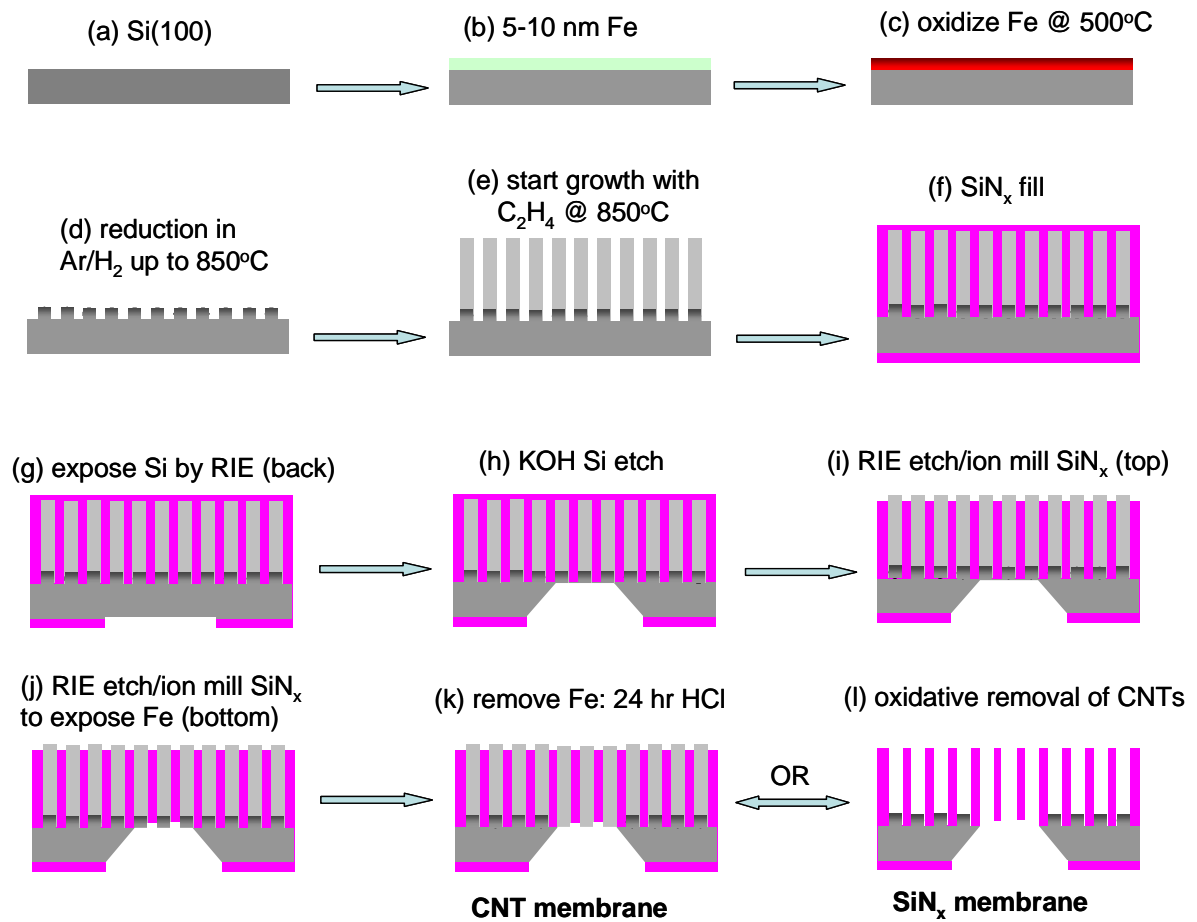


Figure 1. Schematic of CNT membrane fabrication.

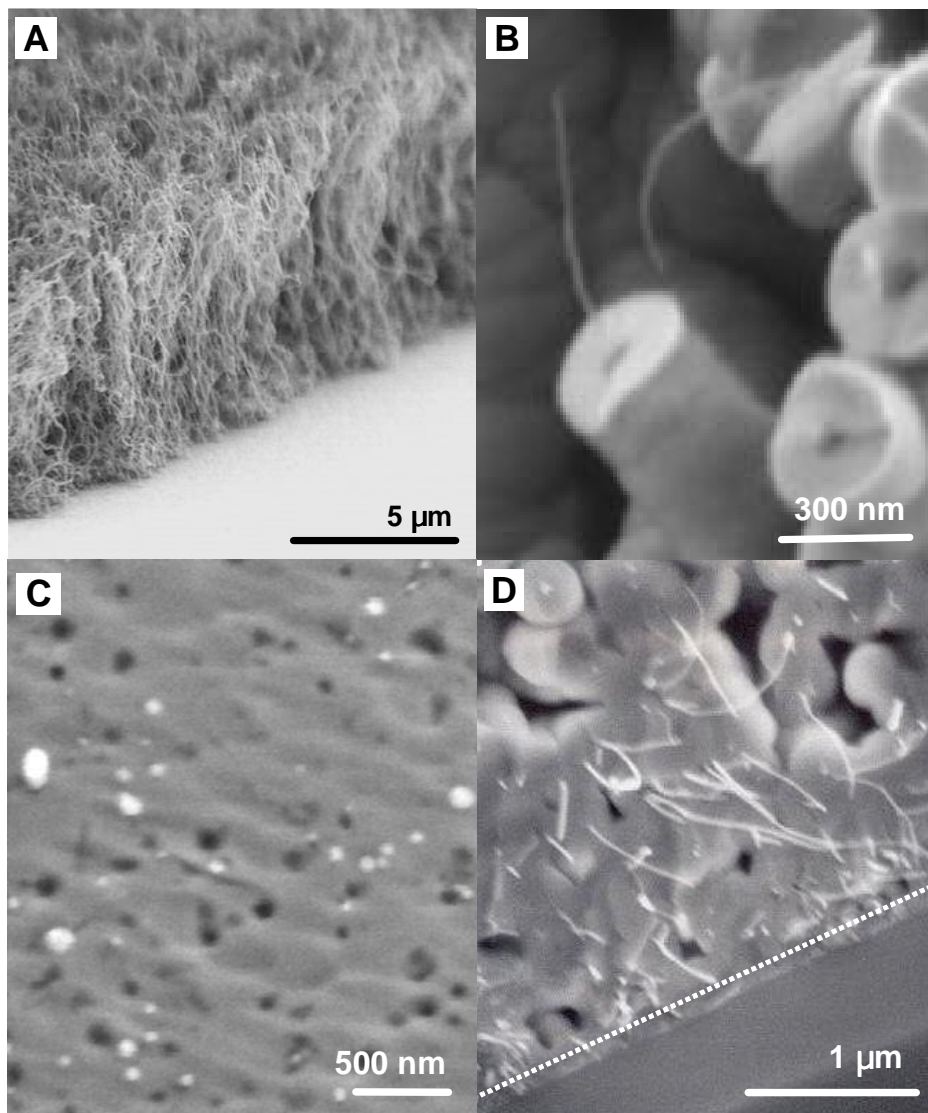


Figure 2. (a) as-grown array of multiwalled CNTs, (b) CNTs encapsulated by a silicon nitride layer, (c) backside of membrane after KOH/ion milling treatment; bright particles were confirmed by EDX to be residual iron not removed after the acid treatment, (d) cross-sectional image of silicon nitride-covered CNTs; the void-free region of the membrane is denoted by the dashed line; individual CNTs can be distinguished as white lines in the image.

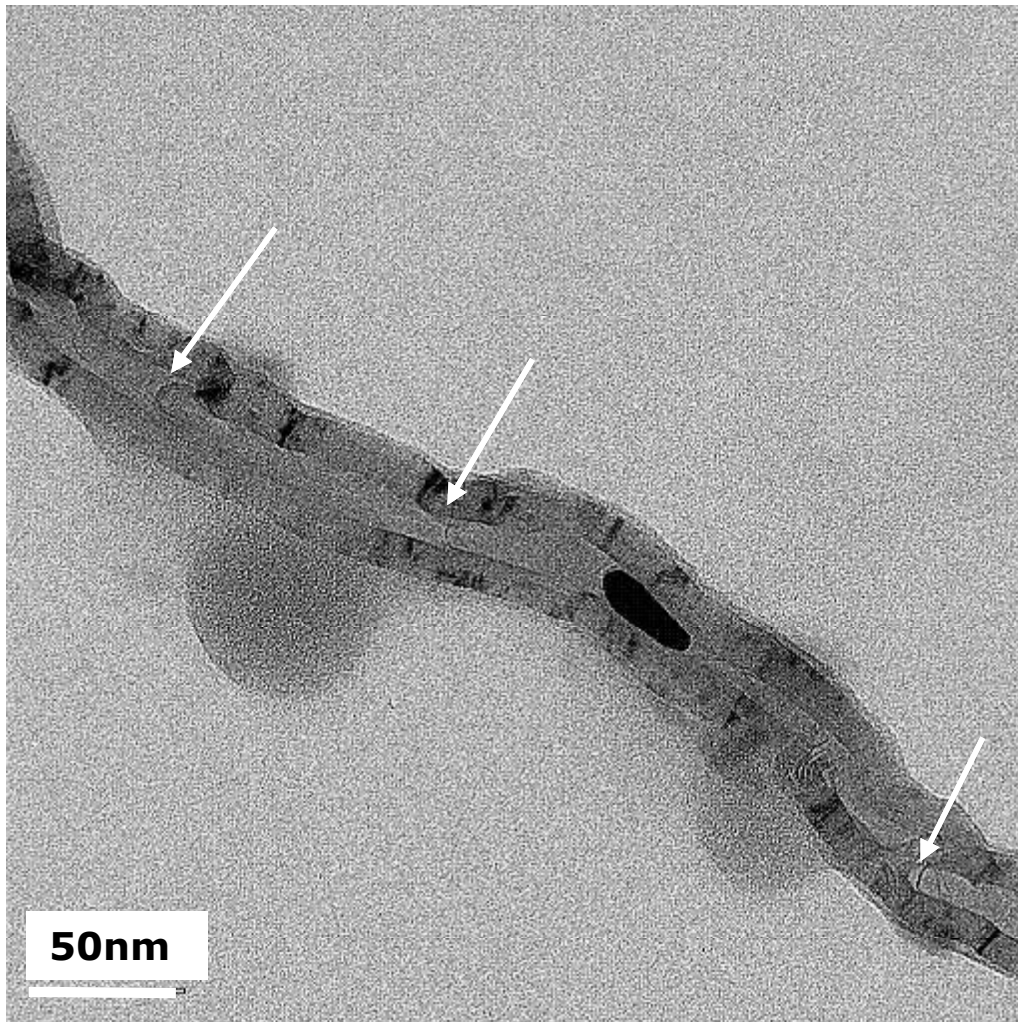


Figure 3. TEM image of a multiwall CNT produced by thermal CVD; arrows indicate graphitic shells that block the interior of the tube, characteristic of “bamboo” CNTs; the dark material is iron catalyst that has migrated to the interior of the tube.

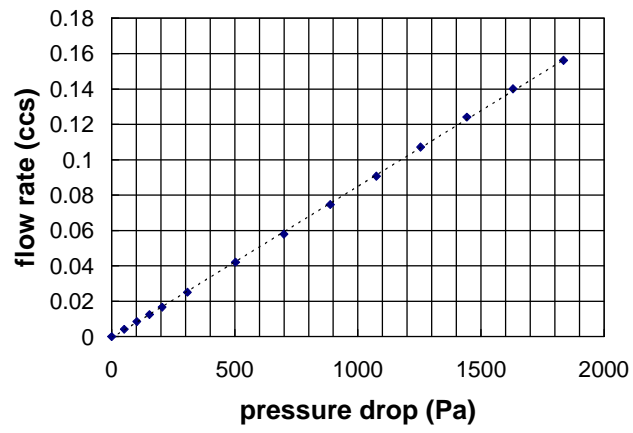


Figure 4. Flow rate versus pressure drop data obtained for a nanoporous silicon nitride membrane.