# Water Transport Through Nanoporous Materials: Porous Silicon and Single Walled Carbon Nanotubes

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*Abstract*—**We report upon the pressure driven water transport through porous silicon (pSi) and single walled carbon nanotube (SWCNT) membranes. Fabrication of the membranes was monitored by AFM and SEM. Water permeability as high as 16926 mm$^3$ cm$^{-2}$ s$^{-1}$ atm$^{-1}$ is found for the pSi membrane. The SWCNT membrane is built upon the pSi membrane and a water permeability of 0.02 mm$^3$ cm$^{-2}$ s$^{-1}$ atm$^{-1}$ is achieved. Performance comparisons to similar CNT membranes are made and future improvements to the system are proposed.**

***Keywords-Carbon nanotube (CNT); porous silicon (pSi); nanoscale water transport; carbon nanotube membrane***

## I. INTRODUCTION

When confined to molecular length scales, fluids display properties that are not observed in the bulk. Nanoconfinement of fluids underlies the functionality of many biological channels, and has motivated investigations into fluid behavior at the nanoscale.

Porous silicon (pSi) is produced through the chemical, photochemical or electrochemical etching of flat, crystalline silicon with fluoride solutions [1]. The pores formed can be in a range of tuneable sizes from micropores (<5 nm) to mesopores (5 – 50 nm) to macropores (>50 nm)[2]. After etching in hydrofluoric acid (HF) the pSi surface is left hydrogen terminated [3], which can be further reacted to produce a range of surface chemistries [4]. Porous silicon membranes, open at both ends, can be generated by either extending the etching time until the whole thickness of the wafer is etched [5] or by using the 'lift off' technique [6] which results in porous membrane detachment from the silicon substrate [7].

To the best of our knowledge mass transport through pSi membranes has been completed only once previously by Cruz et al. [8]. Cruz developed a technique to etch silicon through an entire Si wafer, creating a permeable pSi platform. Nitrogen gas transport was then completed through the membrane where it was found that the permeability changed with pSi film thickness [8]. The major contributing factor that there has been so little work on mass transport through pSi is that the membranes created are very brittle. To overcome this, we have developed a new method to prepare pSi membranes suitable for experimental mass transport.

Since 1991, carbon nanotubes (CNTs) have attracted significant attention due to their unusual mechanical and electrical properties [9-12]. Interest has recently grown toward investigating the flow of fluids through the inner shell of single-walled CNTs (SWCNTs) for investigating flux of water or as size-based chemical or biological separation devices [13-15]. SWCNTs are perfectly suited for such applications over other nanoporous materials because the smoothness and hydrophobicity of the inner walls of SWCNTs leads to an almost frictionless transport of water [16, 17]. At the same time, the size of SWCNTs is much smaller (0.6 – 2 nm) leading to both higher flux and selectivity.

However, experimentally producing CNT platforms suitable for the study of fluid transport has proven to be difficult. The generally adopted approach is to grow an aligned array of CNTs using chemical vapour deposition (CVD), fill in the gaps between the CNTs with polymer (or similar) and finally remove the substrate under the CNTs as well as the tops of the CNTs via an etching technique. This process has been used to create multi-wall carbon nanotube (MWCNT) and double wall carbon nanotube (DWCNT) arrays [18, 19] to investigate flow of gases [14], liquids [13] and for ionic separation [15]. The limitations of this process are the incomplete removal of catalyst particles which may inhibit flow, the use of large radius MWCNT and DWCNTs limiting size-based separation, and the lack of support of the CNT membrane after removal of the substrate, which compromises the stability of the system.

A simple method to produce vertically aligned SWCNTs (VASWCNTs) has recently been developed where pristine SWCNTs are treated with concentrated acid to both shorten the nanotubes and produce carboxylic functionalities on the ends [20]. The carboxylic acid groups are then reacted with either a hydroxylated surface or an aminopropyl triethoxysilane (APTES) layer to form VASWCNT arrays [21-23].

Pressure driven water transport will be examined on both pSi membranes and VASWCNT arrays self-assembled upon a pSi support.

## II. EXPERIMENTAL

### A. *pSi membrane fabrication*

A schematic of the experimental procedure is shown in Figure 1. Permeable pSi substrates were prepared by a two-step electrochemical etching of silicon in a solution of ethanoic hydrofluoric acid (HF). The two-step process involves an initial etching step to create the pores and a final electropolishing step to liberate the porous layer from the silicon wafer. A custom made Teflon cell with an etching area of 1.767 $cm^2$ was used. Prior to etching, the silicon wafer (p-type, 100 orientation, boron doped, 0.0055 – 0.001 Ω cm, Virginia Semiconductor (USA)) was washed with methanol, acetone and DCM and dried under a stream of nitrogen. The first step of etching was carried out at a constant current of 100 mA (Keithley 2425 source meter) for 30 mins in a solution of 3:1 (v/v) 48 % aqueous HF/ethanol (Figure 1 (b)). The HF solution was removed and replaced with a solution of 1:1 (v/v) HF:ethanol for the second etching step. A current of 450 mA was applied for 60 s. The HF solution was then removed and the pSi substrate was washed repeatedly with ethanol, removed from the etching cell and allowed to dry (Figure 1 (c)).

After etching, the free-standing pSi membranes were carefully placed in a tube furnace (Labec, Australia) for 1 h at 400 $^oC$. The membranes were removed from the furnace and allowed to cool and were then either investigated for molecule transport properties or further functionalised with a silane. The pSi membranes were treated with the hydrophobic silane PFDS ((heptadecafluoro - 1, 1, 2, 2 - tetrahydrodecyl)dimethylchlorosilane, Gelest) via the neat silanisation method by placing the membrane within a glass Petri dish, depositing 20 μL of the silane on-top of the membrane, covering the Petri dish and then placing in an oven at 80 $^oC$ for 15 mins [24]. The membrane was then washed repeatedly with ethanol and allowed to dry.

The fragile free-standing pSi membranes were supported by sealing the membrane between two pieces of mica with epoxy. Each piece of mica contained a 0.049 $cm^2$ hole. The mica holders were aligned when adhered to the membrane thus forming an effective open pore area of 0.049 $cm^2$. The support of the mica provided the ability to clamp the pSi membrane into the transport cell without breakage.

### B. *SWCNT membrane fabrication*

20 mg of P2-SWCNTs (Carbon Solutions Inc., USA) (were shortened/cut by adding to 20 mL of 3:1 (v/v) solution of concentrated $H_2SO_4$ (98 %):$HNO_3$(70 %) in an Elma S30 H ultrasonic bath kept at 0 $^oC$ for 8 h. The cutting was stopped after 8 h by adding a 50 fold excess of MilliQ water. The shortened SWCNTs were then filtered under vacuum through a 0.45 μm PTFE (polytetrafluoroethylene) filter (Adelab Scientific, South Australia). The filtered carboxylated SWCNTs were further washed with MilliQ water until a pH of between 5 and 7 was obtained then placed to dry in an oven at 80$^o$C for 12 hours.

A thermally oxidised pSi substrate was placed into a 0.5 % solution of 3-aminopropyl triethoxysilane (APTES, 99 %, Sigma–Aldrich) in anhydrous toluene for 5 min. The substrate was removed from solution, washed by rinsing sequentially in chloroform, acetone and water and dried under a stream of nitrogen. The substrate was then placed into approximately 3 mL of a SWCNT solution containing 0.2 mg $mL^{-1}$ SWCNT, 0.2 mg $mL^{-1}$ DCC in DMSO that had been pre-sonicated for 2 h. The membrane was immersed in the SWCNT solution for 4 h after which it was washed thoroughly with acetone and dried under a stream of nitrogen (Figure 1 (d)).

Styrene (Aldrich) was uninhibited by passing through a column containing activated alumina. Polymerisation was completed by mixing a 1:1.5 (v/v) ratio of styrene to anhydrous toluene with a catalytic amount of phosphorus pentasulfide and reacting at 130$^o$C for 16 h with stirring. The resulting viscous mixture was further diluted with toluene to a concentration of approximately 12.5 g $L^{-1}$.

The polystyrene solution was then dropped onto the pSi-SWCNT surface and spun at 8000 rpm for 2 min (Figure 1 (e)). The top of the polymer layer was removed by water plasma. Water vapour was leaked into an evacuated chamber to a pressure of 0.2 torr, a plasma of 5 mA current was struck and kept for 60 s (Figure 1 (f)). Once completed the pSi-SWCNT-polymer membranes were placed within mica supports as described previously.

### C. *Surface characterisation*

Scanning electron microscopy (SEM) (Helios NanoLab DualBeam, FEI, Adelaide Microscopy) and atomic force microscopy (AFM) were used to characterise the structure of the fabricated pSi membranes. AFM tapping mode images were taken in ambient conditions with a multimode head and a Nanoscope IV controller (Digital Instruments, Veeco, Santa Barbara). Silicon cantilevers (Mikromasch) with fundamental resonance frequency of between 200-400 kHz were used. Images were obtained using a scan rate of 1 Hz with the parameters of set point, amplitude and feedback control optimised manually for each sample. The images presented have been flattened using Nanoscope 6 software.

### D. *Water transport*

Pressure driven water transport experiments were completed using a custom made computer controlled set-up. A syringe pump (Harvard Apparatus) was used to apply pressure to the membrane, the applied pressure was monitored using a Swagelok pressure transducer. The membrane was placed within a commercial membrane holder (Millipore). Water passing through the membrane was collected in a beaker on a balance. The mass and pressure were recorded simultaneously on a LabView program.

## III. RESULTS

### A. *pSi membrane fabrication*

SEM was used to calculate the pore size and depth of pSi membranes created. Figure 2 is an example of a typical image with the mean pore size calculated to be 12.8 nm with a range of 2 to 30 nm. It should be noted that the pores investigated in this study are considerably smaller than those of commonly used materials in these transport experiments (e.g., Anodisc porous alumina, pore size 20 – 200 nm). The depth of the pSi membrane was found to be 70 μm.

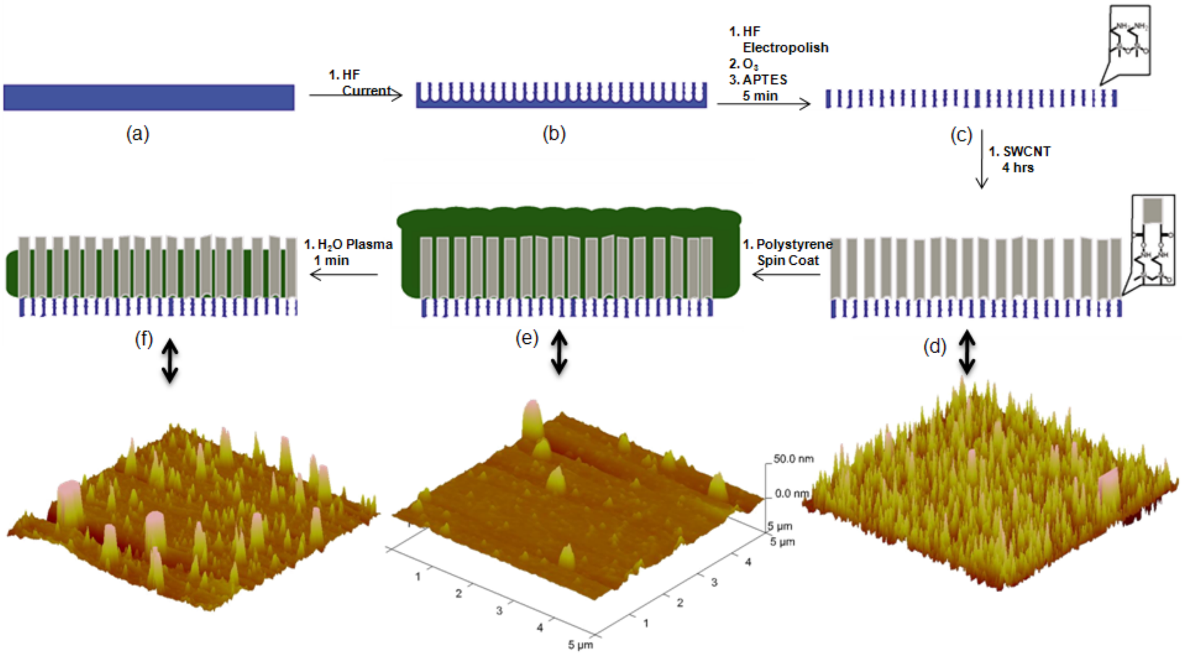

**Figure 1** Schematic detailing fabrication of both pSi and SWCNT membranes. (a) flat silicon is etched with HF to create porous silicon (b) which is then liberated from the surface creating a pSi film (c) this is then used as the pSi membrane for water transport or further functionalised with a silane. The silanised pSi membrane is reacted with shortened SWCNTs which self-assemble to form a VASWCNT array (d) which can then be covered with polystyrene by spin coating (e) the top of the polymer is then removed by water plasma (f) revealing the SWCNT tips.

### *B. Water transport through pSi membrane*

Figure 3 shows the water transport for both oxidized (red) and the hydrophobic PFDS treated (blue) pSi membranes under a constant applied pressure of 0.1 bar. There is a large difference in permeability of the two membranes. The oxidised membrane has a permeability of 16,926 mm$^3$ s$^{-1}$ atm$^{-1}$ cm$^{-2}$ compared to the hydrophobic membrane value of 408 mm$^3$ s$^{-1}$ atm$^{-1}$ cm$^{-2}$. This change in permeability is not only due to the decrease in pore size after silane treatment but also to the low wettability of the membrane resulting in a decrease in water transport. The membranes were found to be able to withstand up to 1.5 atm making it a suitable base for the SWCNT membranes.

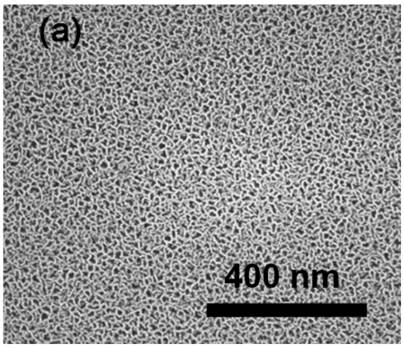

**Figure 2** SEM image of top down view of the pSi membranes investigated

### *C. SWCNT membrane fabrication*

Each step of the SWCNT membrane fabrication was monitored by AFM. Figure 1 (d) shows an AFM of the self-assembled VASWCNT array where the sharp features observed are the SWCNTs. The vertical alignment following this method has been observed and described previously [21].

After the polymer was spun-on, the dense array of VASWCNT is replaced by a rather flat surface with small "bumps" (Figure 1 (e)). This is because the SWCNTs are now covered with polymer. Although some small bumps are still observed, plasma treatment is required to remove the top layer of polymer, when this has been achieved a large number of sharp SWCNT like features are once again observed (Figure 1 (f)). These features are revealed SWCNTs. With revealed SWCNT features on an otherwise polymer covered platform, liquids should now be capable of transporting exclusively through the SWCNT pores.

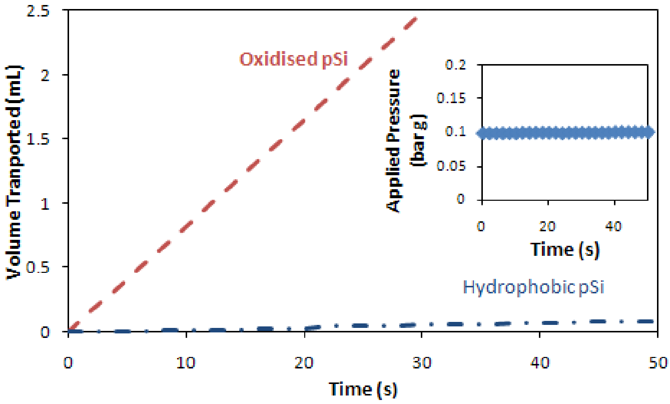

**Figure 3** Pressure driven water transport through (red dashed) oxidised and (blue dash-dotted) PFDS treated pSi membrane; (inset) shows applied pressure.

### *D. Water transport through SWCNT membrane*

The pressure driven transport of water through the SWCNT membranes is shown in Figure 4. The red line shows no water transport over the duration of the experiment due to the SWCNT tips remaining covered in polymer. This control experiment indicates that the polymer layer is impermeable and any transport observed when the SWCNT tips are revealed is from water transporting through the SWCNTs themselves. The blue line shows the water transport through a SWCNT membrane with the SWCNT tips revealed by water plasma. In this instance water transport is recorded with a membrane permeability of 0.02 $mm^3\ s^{-1}\ atm^{-1}\ cm^{-2}$. This value is much lower than that observed for the pSi membrane. The reduction is due to the vast decrease in porosity of the sample. However, when compared to other experimental CNT membranes the permeability calculated is a factor of 100 to 850 times smaller [13, 14], similarly we hypothesise that this is due to the smaller number of available pores and smaller diameter of the SWCNTs. The original VASWCNT on pSi layer has a very high density of SWCNT when compared to the membrane after water plasma, more attention to the polymer encapsulation and top removal is required in order to increase the permeability of the membrane.

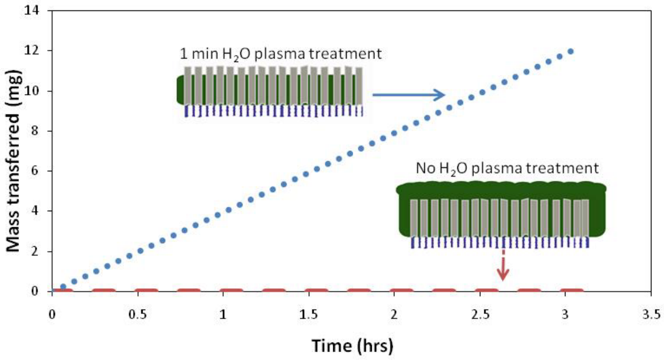

**Figure 4** Pressure driven water transport through SWCNT membrane with (dotted line) SWCNT tips revealed by water plasma and (dashed line) SWCNT tips covered with polymer.

## IV. CONCLUSIONS

Water transport through two different nanoporous membranes has been investigated. Water transport through a pSi membrane has been investigated for the first time. The water transport through the SWCNT membrane was also completed with a low permeability recorded, further work is required to optimize the polymer encapsulation.

## REFERENCES

[1] Canham, L., Properties of Porous Silicon, ed. L. Canham. 1997, London, United Kingdom: The Institution of Electrical Engineers.

[2] Lehmann, V., Electrochemistry of Silicon: Instrumentation, Science, Materials and Applications, ed. Wiley-VCH. 2002, Weinheim, Germany.

[3] Lehmann, V. and U. Gosele, "Porous silicon formation: A quantum wire effect". Applied Physics Letters, vol 58(8): pp. 856-858, 1991

[4] Schmeltzer, J.M. and J.M. Buriak, Recent Developments in the Chemistry and Chemical Applications of Porous Silicon. The Chemistry of Nanomaterials, ed. C.N. Rao, A. Müller, and A.K. Cheetham. 2005. 518-550.

[5] Searson, P.C., "Porous silicon membranes". Applied Physics Letters, vol 59(7): pp. 832-833, 1991

[6] Turner, D.R., "Electropolishing Silicon in Hydrofluoric Acid Solutions". Journal of The Electrochemical Society, vol 105(7): pp. 402-408, 1958

[7] Sagnes, I., A. Halimaoui, G. Vincent, and P.A. Badoz, "Optical absorption evidence of a quantum size effect in porous silicon". Applied Physics Letters, vol 62(10): pp. 1155-1157, 1993

[8] Cruz, S., A. Honig-dOrville, and J. Muller, "Fabrication and optimization of porous silicon substrates for diffusion membrane applications". Journal of The Electrochemical Society, vol 152(6): pp. C418-C424, 2005

[9] Iijima, S., "Helical Microtubules of graphitic carbon". Nature, vol 354: pp. 56, 1991

[10] Hone, J., M.C. Llaguno, M.J. Biercuk, A.T. Johnson, B. Batlogg, Z. Benes, et al., "Thermal properties of carbon nanotubes and nanotube based materials". Applied Physics A:Materials Science & Processing, vol 74: pp. 339, 2002

[11] Wei, B.Q., R. Vajtai, and P.M. Ajayan, "Reliability and current carrying capacity of carbon nanotubes". Applied Physics Letters, vol 79: pp. 1172, 2001

[12] Durkop, T., S.A. Getty, E. Cobas, and M.S. Fuhrer, "Extraordinary Mobility in Semiconducting Carbon Nanotubes". Nano Lett., vol 4(1): pp. 35-39, 2004

[13] Majumder, M., N. Chopra, R. Andrews, and B.J. Hinds, "Enhanced flow in carbon nanotubes". Nature, vol 438: pp. 44, 2005

[14] Holt, J., H. Park, Y. Wang, M. Stadermann, A. Artyukhin, C. Grigoropoulos, et al., "Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes". Science, vol 312: pp. 1034, 2006

[15] Fornasiero, F., H.G. Park, J.K. Holt, M. Stadermann, C.P. Grigoropoulos, A. Noy, et al., "Ion exclusion by sub-2-nm carbon nanotube pores". Proceedings of the National Academy of Sciences: pp. -, 2008

[16] Hummer, G., J.C. Rasaiah, and J.P. Noworyta, "Water conduction through the hydrophobic channel of a carbon nanotube". Nature, vol 414(6860): pp. 188-190, 2001

[17] Kalra, A., S. Garde, and G. Hummer, "Osmotic water transport through carbon nanotube membranes". Proceedings of the National Academy of Sciences, vol 100(18): pp. 10175-10180, 2003

[18] Holt, J.K., A. Noy, T. Huser, D. Eaglesham, and O. Bakajin, "Fabrication of a Carbon Nanotube-Embedded Silicon Nitride Membrane for Studies of Nanometer-Scale Mass Transport". Nano Letters, vol 4(11): pp. 2245-2250, 2004

[19] Hinds, B.J., N. Chopra, T. Rantell, R. Andrews, V. Gavalas, and L.G. Bachas, "Aligned Multiwalled Carbon Nanotube Membranes". Science, vol 303: pp. 62, 2004

[20] Liu, J., A.G. Rinzler, H. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, et al., "Fullerene Pipes". Science, vol 280(5367): pp. 1253-1256, 1998

[21] Shearer, C.J., A. V. Ellis, J.G. Shapter, and N.H. Voelcker, "Chemically Grafted Carbon Nanotube Surface Coverage Gradients". Langmuir, vol 26(23): pp. 18468-18475, 2010

[22] Shearer, C.J., J. Yu, K.M. O'Donnell, L. Thomsen, P.C. Dastoor, J.S. Quinton, and J.G. Shapter, Highly Resilient Field Emission From Aligned Sinlge-Walled Carbon Nanotube Arrays Chemically Attached To n-Type Silicon". Journal of Materials Chemistry, vol 18): pp. 5753-5760, 2008

[23] Yu, J., J.G. Shapter, J.S. Quinton, M.R. Johnston, and D.A. Beattie, "Direct attachment of well-aligned single-walled carbon nanotube architectures to silicon (100) surfaces: a simple approach for device assembly". Physical Chemistry Chemical Physics, vol 9: pp. 510-520, 2007

[24] Fiorilli, S., P. Rivolo, E. Descrovi, C. Ricciardi, L. Pasquardini, L. Lunelli, et al., "Vapor-phase self-assembled monolayers of aminosilane on plasma-activated silicon substrates". Journal of Colloid and Interface Science, vol 321(1): pp. 235-241, 2008

[25] Itkis, M.E., D.E. Perea, S. Niyogi, S.M. Rickard, M.A. Hamon, H. Hu, et al., "Purity Evaluation of As-Prepared Single-Walled Carbon Nanotube Soot by Use of Solution-Phase Near-IR Spectroscopy". Nano Letters, vol 3(3): pp. 309, 2003