Enhanced Fluid Transport Through Carbon Nanopipes

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ABSTRACT

Experimental measurement of fluid flow and diffusion through nanoscale channels is important both for determining how classical theories of fluid dynamics apply at very small length scales and with a view to constructing practical nanofluidic devices. In this study, we observe water flow enhancement of more than 250% in relatively large 271 +/- 31 nm diameter carbon nanopipes with plasma induced surface modification of the carbon walls. Our findings have application in the development of biomedical devices both for sensing and for delivery of therapeutic drugs.

Keywords: nanopipes, nanotubes, carbon, nanofluidics, flow, plasma

1 INTRODUCTION

Understanding the flow of liquids through pipes and channels with dimensions approaching and below 100nm is important both for developing our theoretical models at the nanoscale and for building practical nanofluidic devices [1]. Useful applications are envisaged in process engineering and in nanomedicine. There is now a growing body of evidence based on both theoretical and experimental studies that novel physical phenomena occur when fluids flow through nanoscale pipes, particularly those composed of carbon. Specifically, several recent experimental and theoretical studies [2, 3, 4, 5] have shown that fluids including water can be driven through nanoscale carbon pipes at rates up to five orders of magnitude faster than predicted by the conventional macroscale hydrodynamic equation:

$$Q_0 = \frac{\pi R^4}{8\eta}\frac{\Delta p}{L}$$

This is the Hagen-Poiseuille equation in which Q_0 is the flow rate, R is the pipe radius, η is the viscosity of the fluid, and Δp is the pressure drop between the ends of the pipe with length L. The underlying theory assumes non-slip flow with a parabolic velocity profile across the tube. Molecules of the liquid have zero velocity at the walls and travel fastest at the centre.

The Hagen-Poiseuille equation can be modified by inclusion of a slip coefficient as follows:

$$Q_E = Q_0(1+\frac{4l_s}{R})$$

Where Q_E is the enhanced flow rate resulting from slip at the fluid/wall interface such that molecules of the liquid do have a positive velocity at the wall. The slip coefficient l_s is the distance outside the tube at which the extrapolated parabolic velocity profile tends to zero. It is also known as the slip length.

Recently we have reported results of pressure driven flow measurements for decane, ethanol and water through well aligned carbon nanopipe arrays with a pore diameter of 43 +/- 3 nm [6]. Observed transport rates were more than four orders of magnitude faster than predicted using classical theory. These findings are in accordance with the similar recent work reported by other groups for smaller carbon nanotubes and indicate that enhanced nanofluidic flow regimes can also occur in larger carbon nanopipes produced via CVD (chemical vapour deposition) in carefully prepared AAO (anodic aluminium oxide) templates.

2 FLUID FLOW MEASUREMENTS

In this study we investigated pressure driven flow of water through the inner pores of carbon nanopipes with relatively large diameter 271 ±31 nm. In channels at this scale the influence of interactions at the fluid/wall interface can begin to dominate bulk flow properties. Our interest was to investigate the effect of chemical surface modification of these carbon pipes to determine whether this might modulate transport rates.

2.1 Materials

The nanopipe arrays used in our study were produced using an established CVD method [7, 8, 9] in commercially available AAO templates (Whatman Anodisc 13mm diameter, nominal pore size 200nm). The template consists of a 60 μm thick film of alumina covered with a well-ordered, high density array of open pores produced by electrochemical etching of the original aluminium metal foil. Amorphous carbon was deposited on the template by flowing ethylene gas (30% in helium) for six hours at a rate of 160 sccm at a temperature of 675ºC. SEM (scanning electron microscopy) was used to characterise the size and density of the resulting carbon nanopipe array. Pore

diameter was measured to be 271 ±31 nm and pore density 1.6 ± 0.2 x 10^9 per cm^2. Integrity of the membranes was confirmed by inspection in an optical microscope.

2.2 Experimental Methods

To measure pressure at various flow rates through the pipes, individual membranes were mounted in a brass adapter ring and fixed in place with chemically resistant epoxy (Araldite 2014) to form a pressure-tight seal. The assembly was then fitted inside a stainless steel syringe filter (VWR 402078401)) with a coarse grid metal backing support. Double distilled water, degassed under vacuum and previously filtered through 20nm pores, was then driven through the nanopipe array using a syringe pump (Harvard Apparatus, Model 22 2400-01). Nominal flow rates were verified by periodic weighing of the transported fluid. A stainless steel pressure gauge tee (Upchurch Scientific, part number U-433) was located between the syringe pump and the filter holder to allow connection of a pressure sensor (Omega, PX-603-500G5V). Fluid pressure behind the membrane was monitored using a digital panel meter (Omega, DP25B-S-230) calibrated to kPa using a mercury manometer and reading zero at one atmosphere. The stabilized pressure at five different flow rates was measured and standardized to a membrane area of 1 cm^2 before calculating averages and standard deviations. A schematic of the experimental system is shown in Figure 1 below.

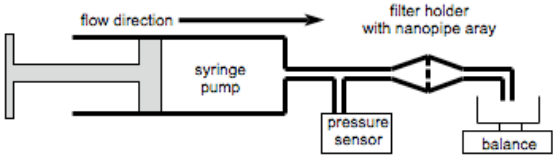

Figure 1. Schematic diagram showing experimental setup for measuring pressure at a series of imposed flow rates.

To assess the effect of chemical surface modification of the carbon nanopipes on water transport rates, intact carbon nanomembranes were exposed to an air plasma for 30 seconds. The instrument used was a March Plasmod running at maximum power (nominally 150W) and at an RF frequency of 13.54 MHz. Wettability is a measure of surface chemistry and the contact angle for a 0.005ml drop of distilled water was compared for the treated and untreated halves of the membrane. The water drop had a high contact angle (~ 110º) on the untreated carbon. On the treated membrane it immediately and completely wetted the surface (contact angle 0º). In other words, brief exposure to air plasma caused the carbon surface to change from somewhat hydrophobic to highly hydrophilic.

To determine the effect of this surface modification on fluid flow, three pairs of treated and untreated membrane fragments were mounted in brass adapters. The pressure driven flow of water was then measured in the manner previously described. Good quality data was obtained for all three treated samples and for two of the controls. Results for the remaining control was discarded due to pressure-induced cracking. This precluded plotting of standard deviations for this series.

2.3 Results

The preliminary data are presented in Figure 3. An average flow enhancement of 250% was seen for the carbon membranes exposed to air plasma. Preliminary XPS data confirms a marked increase in OH and COOH groups in the treated samples compared to the untreated controls.

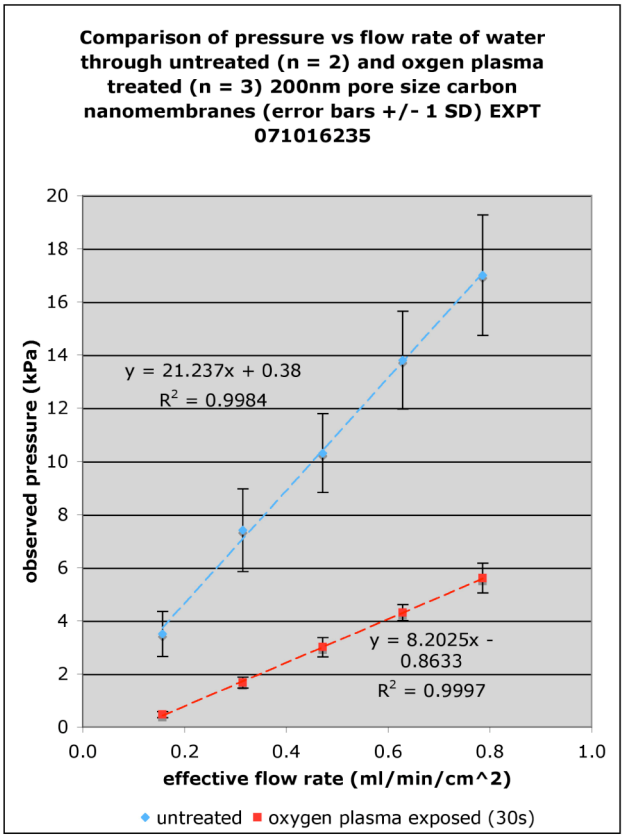

Figure 2. Plot of imposed flow rate against observed pressure for water passing through plasma treated carbon nanopipe arrays compared to untreated controls. The flow rate through the surface modified samples is > 250% faster.

2.4 Discussion

A possible explanation of the observed flow enhancement is that plasma treatment might simply have enlarged the physical size of the pores. Plasma etching is a

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well know technique in the semiconductor industry and exposure to oxygen plasma can quickly remove organic material including elemental carbon. To test this possibility, the treated membranes used in the experiment were examined using SEM and compared with the untreated samples to see if there was evidence of pore widening. An example micrograph is show below in Figure 3.

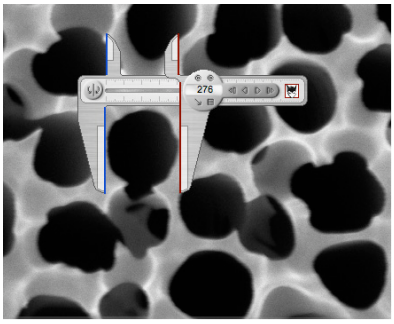

Figure 3. SEM micrograph of plasma treated carbon nanopipe array showing one surface of the membrane with open pores. The caliper scale is in nm.

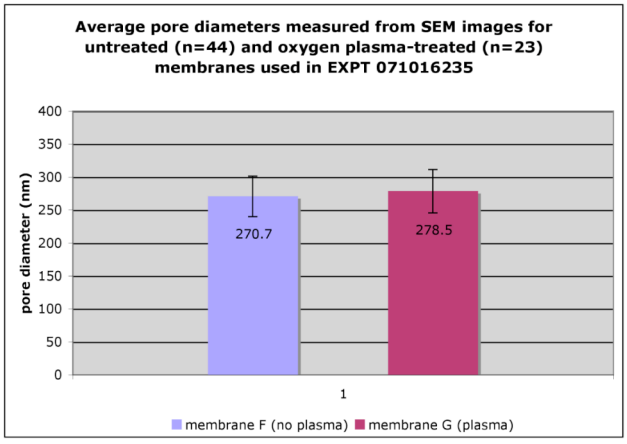

Figure 4. Chart comparing measured diameters of plasma treated and untreated carbon nanopipe pores.

As can be seen from Figure 4 above, there was only a small (< 3%) difference between average pore diameters of the treated and untreated samples. Furthermore this difference was well within one standard deviation of both sets of values and cannot be considered significant. Even if it did reflect a real difference, the resulting increase in flow due to the wider channel would account for less than one tenth of the observed enhancement.

We therefore consider more likely the alternative explanation that increased hydrophilicity of the carbon nanopipes has changed interaction with the water resulting in the observed raised flow rate. Simulation studies and more detailed XPS analysis are currently underway to elucidate the possible mechanisms.

3 CONCLUSIONS

Transport rates of pressure-driven water through 271 ±31 nm carbon nanopipes was measured and flow enhancement of more than 250% was found for carbon surfaces chemically modified by prior exposure to an air plasma. XPS analysis of the treated and untreated surfaces confirms a substantial increase in OH and COOH groups on the plasma treated nanopipes, consistent with an increase in hydrophilicity. This previously unreported method of achieving flow enhancement may be useful in designing future nanofluidic devices.

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