Anomalous Decline of Water Transport in Covalently Modified Carbon Nanotube Membranes

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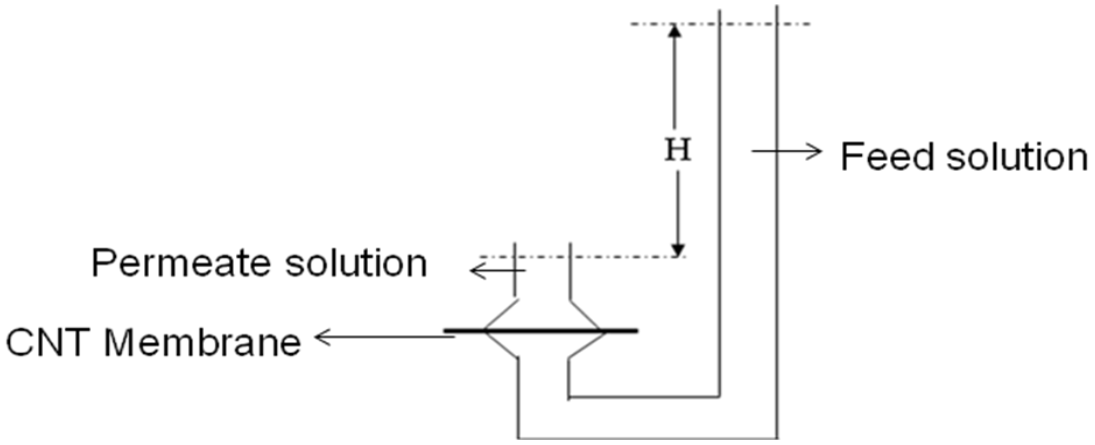
S.1 Method of Measurement



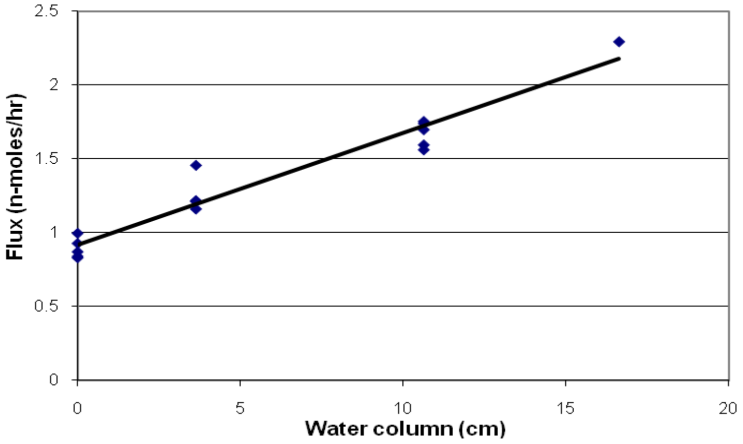


Figure S1. Schematic of the experimental set-up to study pressure driven water transport using a UV-active probe molecule Ru(bipy)$_3^{2+}$ as the feed solution. The extra height of the feed solution (H), provides the requisite pressure for measuring the convective transport properties of carbon nanotube membranes. Below: Plot of experimental data of pressure driven transport in CNT membranes.

S.2 Electrosmotic Flow in Functionalized Carbon Nanotube Membranes

For electrosmotic transport studies in the cross-potential mode, the experimental set-up shown in figure S2 was used. In this case, the working electrode was placed in the permeate cell. This allowed an electrical potential gradient to be applied across the membrane allowing for experimentally studying electrically-facilitated transport across the membrane. Constant potential was applied using Potentiostat/Galvanostat Model 263, of Princeton Applied Research and the potentials reported are w.r.t. Ag/AgCl (sat. KCl) electrode. Concentration of Ru(bipy)$_3^{2+}$ and MV^{2+} in the permeate was measured after 15-40 hours of diffusion experiments using UV-vis Spectrophotometer (USB-ISS-UV-vis, Ocean Optics Inc.). In order to obtain consistent measurements in the UV-vis spectrophotometer, it was necessary for long measurement times so that sufficient amounts of the probe molecules had permeated. The MV^{2+} flux was calculated from the peak at 260 nm.

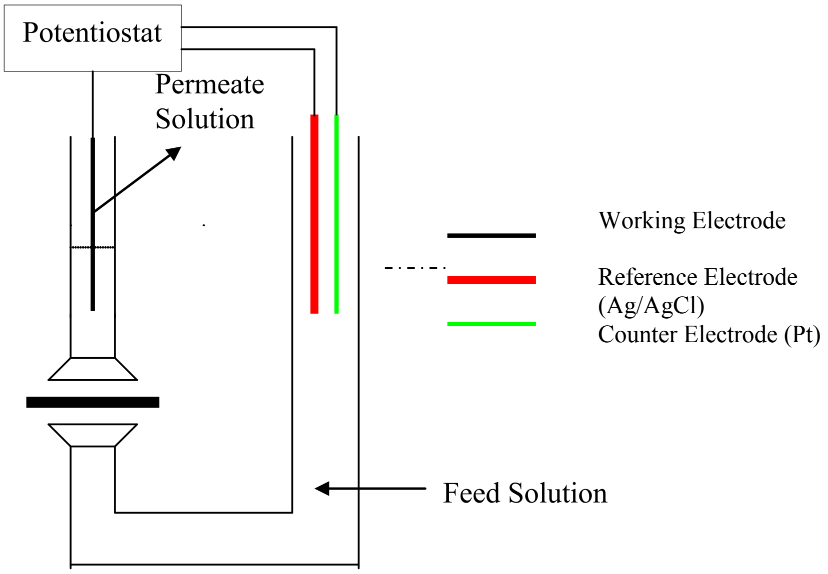


Figure S2.1 Experimental set-up for studying electro-phoretic and electro-osmotic transport across carbon nanotube membranes. The permeate concentration is measured as a function of time by UV-vis spectroscopy. The experiments are carried out potentiostatically using a Potentiostat/Galvanostat (Model 263A, Princeton Applied Research). Both the working and counter electrode are Pt wires and the reference electrode is an Ag/AgCl (sat. KCl) electrode.

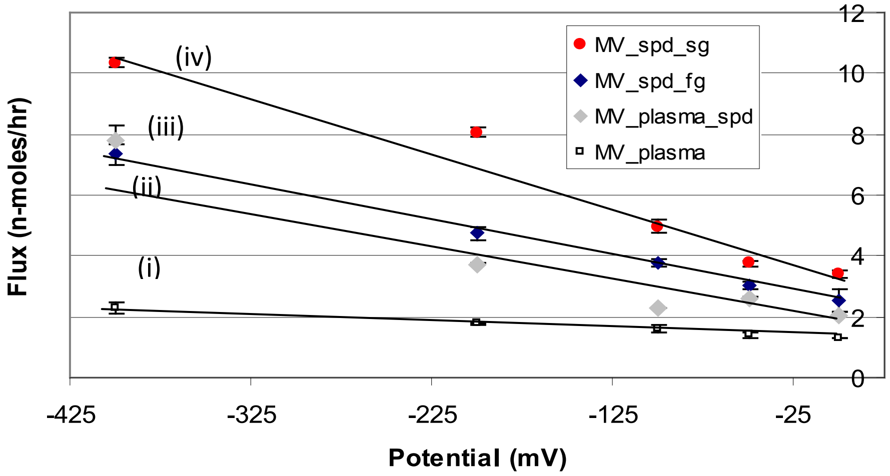


Figure S2.2 Methyl viologen flux through carbon nanotube membrane as a function of applied negative potential to the working electrode with different functionalization treatments. The feed solution is 5 mM in $Ru(bipy)_3^{+2}$, 5 mM in MV^{+2} and 0.1 (M) in KCl. The permeate cell contains 0.1M KCl solution. Lines are added as an aid to eye.

The membranes are: (i) as-made without any functionalization (ii) with spacer-dye functionalization (iii) flow grafted and spacer-dye functionalized (iv) core-grafted with spacer dye functionalization. Note that with increasing functionalization (i) through (iv), the electrosmotically driven flow of the cations increases indicating that the functionalization does not plug the pores. This observation is consistent with increase in the surface bound charges leading to an increased zeta-potential and a greater double layer drag on the probe molecule. However, what is anomalous and unique to nanotubes transport is that the pressure driven water flux decreases with increasing hydrophilicty.

S.3 Simulations of Fluid Flow

Two families of periodic simulation system both containing a 7nm diameter (50,50) armchair CNT were used in molecular dynamics simulations to study fluid flow. The first family was used to study the influence of polarity in a smooth CNT and involved a 6nm long CNT with a 24 Å slab of TIP3P water at either end (Figure 3A). Simulations were conducted with (i) all carbon atoms neutral and (ii) a positive charge added to 1/8 of the carbon atoms and a negative charge of equal magnitude added to an additional 1/8 of the carbon atoms. Charges from 0.1 to 0.9 *e* were examined. In the second family of simulation systems, a 12 nm long CNT surrounded by a 54 Å slab of water an including 0.1 M KCl was utilised as shown in figure 3B to allow for the effects of functionalising the CNT tips to be examined. Simulations were conducted both without the addition of functional molecules and with 5 functional molecules attached to each end of the CNT to mimic the experimental conditions.

Following our previous studies [1] the CNT atoms were taken as aromatic carbon (type 'CA") in the CHARMM27 force field [2]. Charges on the atoms in the functional molecules were determined by first performing geometry optimisation using a 6-31+G* basis set using Gaussian [3] and then calculating point charges using the Merz-Kollman electrostatic fitting method [4]. Equilibrium bond lengths, angles and dihedrals were taken from the quantum mechanical calculations while the force constants for bonds and van der Waals parameters were determined from comparison with similar atom types in the CHARMM27 force field.

A hydrostatic pressure difference was created across the membrane using the method of Zhu et al [5] in which a constant force, f, is applied in the direction of the CNT axis to oxygen atoms in water molecules in 10 Å wide layers at the very top and bottom of the simulation system. Due to the periodic nature of the system this creates a region of water at high pressure on one side of the CNT and lower pressure on the opposite side with a total pressure difference given by $\Delta P = nf/A$, where n is the average numbers of atoms to which the fore is applied and A is the cross sectional area of the simulation (perpendicular to the CNT axis). Water was excluded from the areas on the sides of CNTs through the addition of a Lennard-Jones interaction along the plane level with each end of the CNT, with parameters chosen to mimic those with a sheet of carbon atoms. Initial equilibration was conducted prior to the addition of hydrostatic pressure under constant pressure (1 atm) and temperature (300K), before subsequent simulations were run with constant system volume. All simulations were conducted using NAMD [6] using a 1fs timestep with periodic boundary conditions a 12 Å cut off for van der Waals interactions and using a particle mesh Ewald scheme for calculating electrostatic interactions.

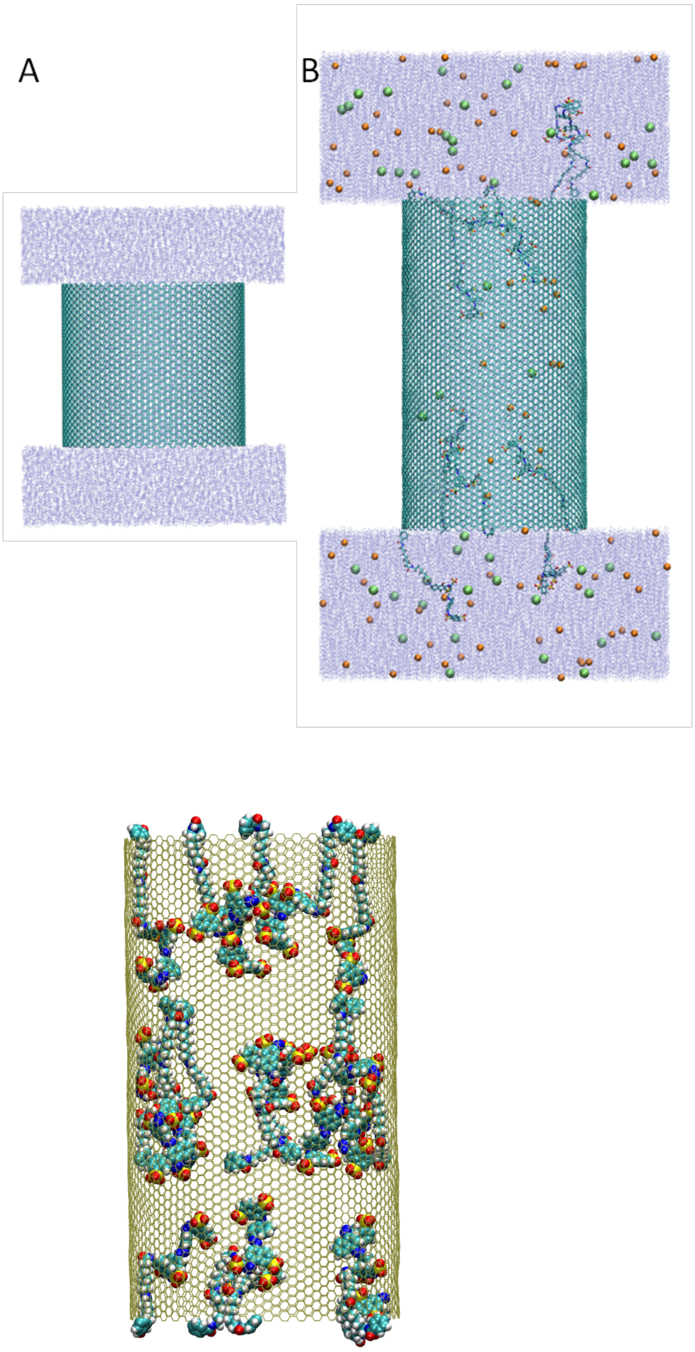


Figure S3 A snapshot of the simulation systems used to study fluid flow in (A) smooth polar CNTs, (B) tip functionalised and (C) core functionalised CNTs. Water is not shown in C so as not to obscure the locations of the functional groups attached to the CNT.

S.3 Additional Simulation Data

As previously reported water forms layers near the CNT walls as shown in figure S4. The relationship between the charge on the polar atoms in the smooth CNTs and the average van der Waals and electrostatic interaction of water molecules adjacent to the CNT walls is shown in figure S5. As expected, the total electrostatic interaction rapidly increases with increasing CNT polarity. The van der Waals interaction, however, slightly decrease as the water molecules reorientate to point their dipoles toward the polar carbon atoms, rather than lying flat against the CNT surface.

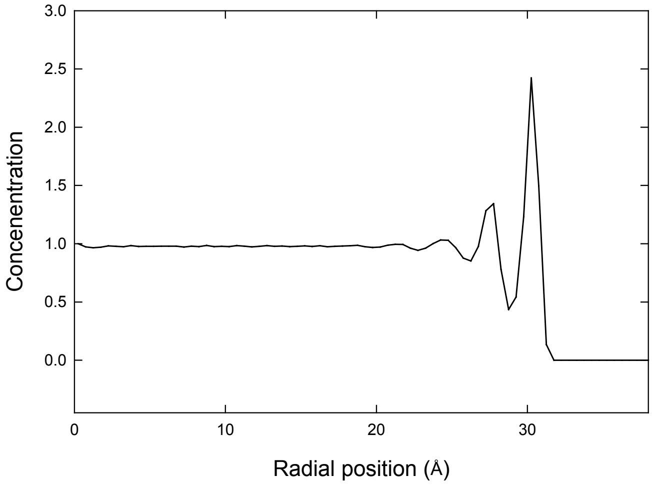


Figure S4 The concentration of water (normalised to the concentration in the centre of the CNT) is plotted against the radial position in the nanotube.

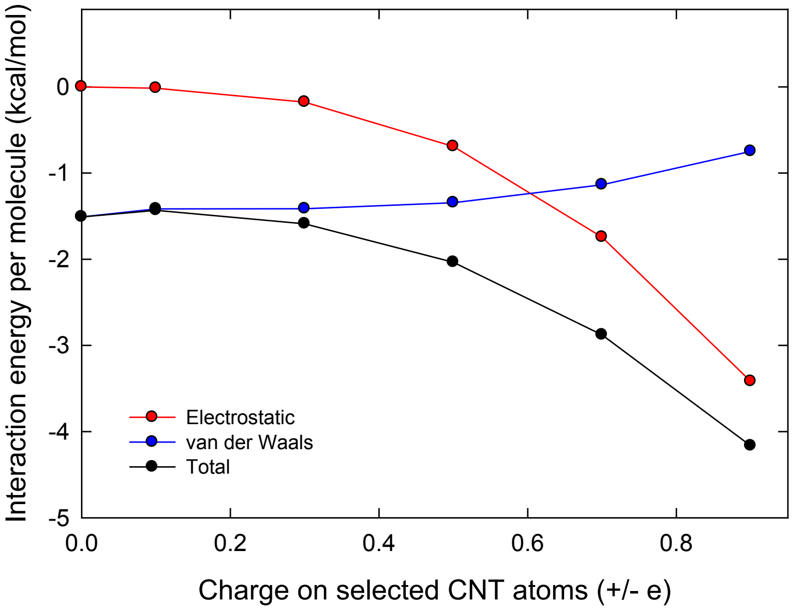


Figure S5 The average total, electrostatic and van der Waals interaction energy of each water molecule adjacent to the CNT walls with the CNT is plotted against the charge on the polar atoms in the CNT.

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Supplemental Information (for review only)

Membrane type	**Flow velocity at 1 bar (cm/s)**	**Enhancement factor**	**Normalized diffusive flux**
As-made	10.9(±5.1)	4.6 (±2.1) × 10^4	1
CNT-tip	4.7 (±0.7) ×10^{-2}	2 (±0.3) × 10^2	0.93
CNT-core	< 1.26 × 10^{-3}	< 5.3	1.03

Table: Summary of convection flow velocities obtained in different functionalized carbon nanotube membranes and normalized diffusive flux (data to be published in ACS Nano)