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Anomalous decline of water transport in covalently modified carbon nanotube membranes†

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Carbon nanotube membranes have been shown to rapidly transport liquids; but progressive hydrophilic modification—contrary to expectations—induces a drastic reduction of water flow. Enhanced electrostatic interaction and the disruption of the mechanically smooth graphitic walls is the determinant of this behavior. These results have critical implications in the design of nanofluidic devices.

Liquid transport through the inner core of carbon nanotubes (CNTs) has recently attracted considerable attention from theoretical as well as experimental standpoints.[1,2] Similar to biological channels such as aquaporin, these atomically smooth graphitic pores permit fluids to flow with extreme rapidity which is not observed in other nano-porous systems.[3–9] This has given promise to novel technologies in desalination, water-purification, drug delivery, nanofluidics and nanofiltration. Adaptive and functional groups placed on the carbon nanotubes are capable of imparting selectivity. For example, diffusive transport through the nanotubes can be modulated through the addition of charged functional groups *via* carbodiimide mediated coupling to COOH groups at the nanotube ends.[10] Additional COOH anchoring groups can also be grafted in the graphitic interiors of the CNTs by electroreduction of 4-carboxy phenyl diazonium tetrafluroborate.[11] Suitably functionalized carbon nanotube membranes demonstrate voltage-gated transport[12] or electro-osmotically controlled fluid flow.[5] However, we have recently observed that progressive hydrophilic functionalization of CNT membranes drastically reduces convective (pressure-driven) water flow[13]-a behavior which is counterintuitive to transport in conventional porous films. Here, through detailed molecular dynamics simulations under conditions similar to the experiments, we provide insights into the mechanism of this anomalous observation and note the implications of this behaviour.

To align the readers, we briefly revisit the key experimental steps for progressive functionalization of the tips and the core of the CNTs of the aligned CNT membranes. To modify the entire core of the CNTs, the membrane was grafted electrochemically using diazonium chemistry utilizing our previously established protocols.[10,12] Electrochemical capacitance measurements confirmed that the functional density of COOH groups increased by more than two fold after this process.[11] The membrane was subsequently functionalized with a polypeptide spacer and a quadvalent sulphonated anionic dye molecule shown in Fig. 1. The different approaches to functionalization yielded three different kinds of carbon nanotube membranes: (i) as-made plasma oxidized membranes with a few carboxylic acid at the CNT tips without further manipulation, (ii) tip-functionalized membranes achieved through chemical modification of the carboxylic acid groups of the as-made membrane, (iii) core-functionalized membranes through chemical modification of the diazo-grafted CNT membrane. The bulky anionic functional groups were chosen not only to impart charged groups but also enhance the surface roughness of the graphitic surfaces.

In our prior diffusion experiments to explore the influence of 'gate-keeper' molecules on transport in CNT membranes, a permeate cell was placed in a U-tube. A feed solution containing 5 mM $Ru(bipy)_3^{2+}$ as the probe molecule was maintained at the same level on either side of the membrane to ensure minimum pressure driven flux.[10] However, in these experiments the extra

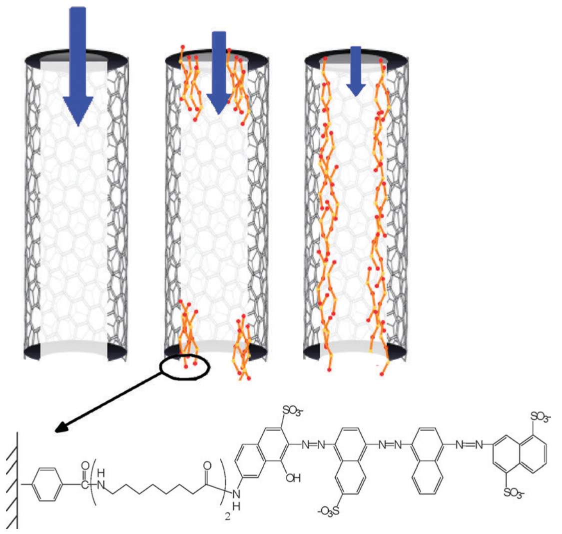

Fig. 1 Illustration of the position of the functional molecule in the CNT-tip and CNT-core fluidic channels and chemical structure of the molecule.

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height of the feed column provided the driving force for convective flow. The total flux of the probe molecule in convective-diffusive transport can be expressed as the sum of the diffusive and the convective flux by the following equation:

$$J_T = J_D + J_C = DA_p\frac{dc}{dx} + vA_pC$$

Here, D is the diffusivity of the probe molecule-Ru(bipy)$_3^{2+}$, A_p is the available pore area, C is the concentration of the feed solution, dc/dx is the concentration gradient across the membrane, and v is the convective velocity of transport. In the diffusive mode, the permeable pore area (A_p) can be estimated from J_D with the assumption of bulk diffusivity of the probe (Ru(bipy)$_3^{2+}$) in the CNT channels.[13] The flow velocity of the Ru(bipy)$_3^{2+}$ containing water (measured by monitoring UV-vis absorbance from the probe molecule) in the as-made membrane (11 ± 5 cm s^{-1} at 1 bar) is consistent with the flow velocity of pure water measured in our previous experiments.[2] In contrast, the no-slip flow velocity expected from the Haagen–Poiseuille equation is about 5×10^{-4} cm s^{-1}. Similar experiments showed that the flow velocity of 5 mM Ru(bipy)$_3^{2+}$ solution had decreased to 0.04 (±0.007) cm s^{-1} for tip-functionalized CNT membranes. More drastically, the core-grafted CNT membrane had no detectable pressure driven flow. Consistently, throughout these experiments, the diffusive flux does not significantly change from their as-made state indicating that functionalization does not plug the pores, rather modifies the boundary layer interaction between the permeating species and CNT walls. Further evidence is provided by the increase in electro-osmotic flow with an increase in surface bound charges as is obtained through progressive chemical functionalization (see supplementary information†). This enhancement of electro-osmotic flow is consistent with an increased zeta-potential at the nanotube walls and a subsequent larger density of counter-ion transport. However, what is anomalous as well as unique here is the rapid decline in pressure driven water transport seen with increasing numbers of charged hydrophilic groups in the pore.

This rapid decline in convective water transport in CNT fluidics can arise from two sources, namely: (i) increased roughness of the CNT walls and/or (ii) electrostatic interaction between the polar water molecules and the polar CNT walls. While Joseph *et al.*[14] have demonstrated in simulations that transport rates are lower in carbon nanotubes with mechanically rough surface, we conducted MD simulations to understand if surface charges/polarized walls also affect water flow. To do this, MD simulations were conducted with a hydrostatic pressure difference across both nonpolar CNTs and a range of CNTs with polar surfaces obtained by adding an equal number of positive and negative charges of magnitude (specified in each of the figures captions) to 1/4 of the atoms comprising the CNT. Although the nanotubes for the experiments were ~7 nm in diameter and ~100 μm in length, the simulations were conducted with nanotubes of the same diameter but of much shorter length (6.2 nm) for computational efficiency using a TIP3P water model.

Fig. 2 shows the axial flow velocity profiles of water inside the nanotubes as the polarization of the CNT walls is increased while the smoothness of the pore wall is unchanged. It is clearly observed that polarization of the nanotubes changes the velocity profile from the 'plug-flow' profile observed in pristine carbon nanotubes to the more conventional 'parabolic-flow'. In the as-made (unfunctionalized) case, the water molecules do not have significantly preferred positions in the nanotubes, thus Fig. 3A and B show a uniform concentration of oxygen and hydrogen near the CNT walls. Fig. 3E shows a representative snapshot from the MD simulation highlighting the relatively unstructured arrangement of the individual water molecules relative to the nanotube walls. When the CNT walls are polar, however, there is a strong interaction between the water molecules and the charged atoms along the wall (see supplemental section†). In the most polar case considered, for example, the interaction energy between each water molecule and the CNT is nearly 3 times that for the non polar CNT. As a consequence of the strong electrostatic interactions, the hydrogen atoms on the water like to point directly at the negative charges on the CNT as seen in Fig. 3D and F. Oxygen also sits above these hydrogen atoms (Fig. 3C) as the oxygen, hydrogen and negative atom on the CNT all form a line perpendicular to the CNT wall. Oxygen can also be found above the positive charges on the CNT unlike hydrogen. A snapshot of the polar case is shown in Fig. 3F and an ordered arrangement is observed with the hydrogen atoms lying very close to the CNT. Increasing the strength of interaction reduces the movement of the water molecules relative to the CNT, yielding the 'parabolic-flow' profiles seen in Fig. 2 and reducing the total water flow as has been seen in simulations of narrow functionalized CNTs.[15]

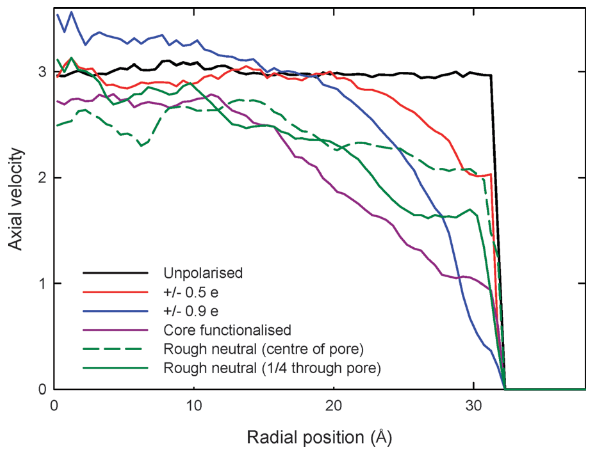

Fig. 2 Simulated flow profile in the unpolarized, polarized and functionalized CNTs.

To understand how the length of the CNT affects the water flux we conducted additional simulations in CNTs twice the length of those described in the previous simulations. In the case of the pristine CNT, doubling the length of the pore has no influence on the water flux as seen in Table 1, due to the limited interactions between water and the CNT, indicating that in this case the flux is independent of nanotube length. For the polar CNTs, however, a different result is obtained. In this case, doubling the length of the tube decreases the water flux by a further 10% compared to pristine CNT. Assuming that each doubling of CNT length creates a similar 10% decrease in flux, and noting that the CNTs used in the experimental platform are about 50 000 times longer than those used in the simulations, the flow decrease seen in the simulations is sufficient to explain the decreases seen in the experimental results.

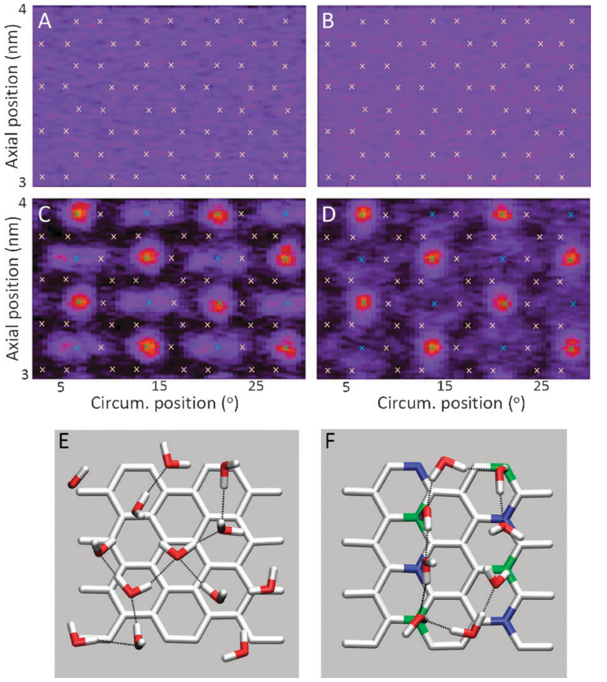

Fig. 3 Concentration of hydrogen or oxygen in the layer adjacent to the CNT plotted on the face of the CNT using the axial position (z) and the circumference position (defined by the angle around the tube). A is oxygen in unfunctionalized CNT; B is hydrogen in unfunctionalized CNT; C is oxygen in polar CNT (±0.9 e); D is hydrogen in polar CNT (±0.9 e). The positions of the carbon atoms are shown by the crosses in figures A to D. In figures C, D and F, green represents the negative charges on CNT atoms and blue the positive charges.

To further see the effect of both the addition of charged groups and surface roughness to the pores we also carried out simulations with 6.2 and 12.4 nm long CNTs explicitly functionalized with the molecule shown in Fig. 1b either at the tip, or throughout the length of the pore. To further differentiate between the addition of surface roughness and charge/polarity additional simulations are conducted with functionalized CNTS, but with all atomic partial charges on the functional molecule set to zero such that no electrostatic interactions are present. In either case, the functional molecules tend to lie on the surface of the CNT rather than projecting into the pore (see supplemental Fig. S3†). Increasing surface roughness has a dramatic affect on the water flow, producing something between the 'parabolic' and 'plug-flow' profile (shown in Fig. 2) due to the increasing turbulence of the water in the pore and destabilizing the structure of the water near the interface with the CNT that has been shown to be critical in allowing rapid transport.[14] Evidence of this turbulence can be seen by comparing the flow profile at different heights in the pore as water has to move in different directions to move around the functional groups.

Table 1 Simulated flux of water molecules through CNTs of 7 nm diameter with varying conditions of polarities, surface roughness and length as a percentage of flux in the pristine nanotube

CNT type	Flux as % of pristine CNT
6.2 nm long, unpolarised (pristine)	100 ± 1
12.4 nm long, unpolarised	100 ± 2
6.2 nm long, polarised	73 ± 2
12.4 nm long, polarised	63 ± 2
6.2 nm long, core functionalised, neutral	78 ± 2
6.2 nm long, core functionalised, polar	74 ± 2
12.4 nm long, core functionalised, neutral	73 ± 2
12.4 nm long, core functionalised, polar	68 ± 2

The inclusion of electrostatic interactions in addition to surface roughness further decreases the water flow as shown in Table 1. The charged functional groups increase the average strength of interaction between the pore and the water molecules (1.66 kcal mol^{-1} per water molecule) compared to the unfunctionalised CNT (0.34 kcal mol^{-1}) due to the presence of electrostatic interactions and a larger interacting surface area. Similar to the polar CNTs, the water flow is further decreased with increasing CNT length.

Many applications of liquid flux in CNTs are likely to require chemical functionalisation of the CNTs in order to obtain selective and controlled transport. These results suggest that any such modification is likely to reduce the rate of transport in the CNTs and thus raise a challenging question: how do we achieve the goals of both high selectivity and high flow in carbon nanotube fluidics which is so easily obtained in biological ion channels? Nevertheless, these simulations explain why progressive hydrophilic functionalization and the resultant change in nanoscale environment reduces water transport in carbon nanotubes. Moreover it also validates the claim that the enhanced water flow characteristics of liquids in CNTs arises from both the mechanical and electrical smoothness of the interior of the pores and that disruption of either factor drastically reduces the remarkable fluid flow properties of the nanotubes.

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