Carbon Nanopipes for Nanofluidic Devices and *In-situ* Fluid Studies

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Project Objectives

The processes that govern fluid transport in pipes are well understood for diameters in the range of micrometers and above. As the diameters diminish (e.g. in the range of a few nanometers), the roles of surface tension and capillarity seem to vary. Thus, the expected promise of carbon nanotubes (CNT, 1-10 nm inner diameter) and nanopipes (CNP, 50-200 nm inner diameter) in technological applications is in urgent need of a well-documented, basic understanding of such forces, especially since no consistent experimental data have been collected until recently. We have investigated the liquid/vapor distribution in nanotubes, the interaction of fluids with the tube walls, and the effect of hydrothermal treatment on the surface chemistry of carbon nanotubes.[1,2] On this basis, we are developing a research program that will thoroughly explore the various aspects of phase interfacing in a number of different nanotube situations. Hydrothermal and CVD-grown CNP will be examined. Fluid behavior, chemical modification, and opening of the CNP using bipolar electrochemistry will be investigated. The experimental work will be supplemented by modeling work based on parallel molecular dynamics simulations. Finally, we will design nanotube-based nanofluidic devices, which may find applications in cellular probes, lab-on-a-chip manufacturing, electrochemical cells, and beyond.

Results

1. Fluid Behavior in Carbon Nanotubes

Fig. 1 shows a sequence of environmental scanning electron microscopy (ESEM) images obtained when partial pressure of water in the ESEM chamber was gradually raised in a controlled manner, while observing a single open carbon CNP, which was originally empty (no fluid). These experiments were performed with the sample cooled to 4°C, in order to create environmental conditions corresponding to liquid/gas equilibrium (the water saturation temperature at a pressure of 6 Torr is slightly below 4°C). The complex gas/liquid interface seen in Fig. 1a resembles the interfaces visualized in hydrothermal nanotubes[3,4] containing a water-based fluid and subjected to sustained heating (Fig. 2). This resemblance suggests that both fluids are in a vigorous evaporating state, creating temperature gradients, which in turn allow the formation of such complex transient interfaces. The energy of the electron beam serves as the heat source in both cases. Note that Fig. 1 corresponds to an open CNP in which pure water is condensed at low pressure, while Fig. 2 corresponds to a capped hydrothermal CNP containing an aqueous liquid with small amounts of CO_2 and possibly CH_4[5] above atmospheric pressure.

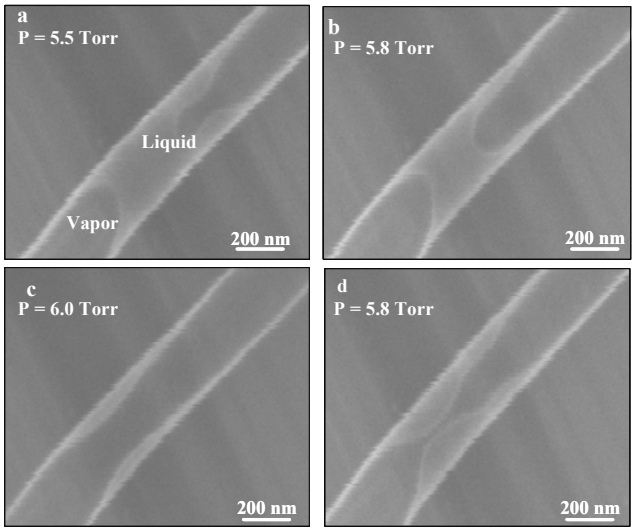

Fig. 1: Sequence of images obtained in the ESEM using amorphous hydrophilic CVD CNP. The jagged appearance of the CNP is due to a high scanning rate. Note the liquid-volume reduction during pressure buildup (a-c), and volume recovery during pressure decrease (c-d). This trend is counterintuitive, and exemplifies the challenges to be faced in the proposed work.

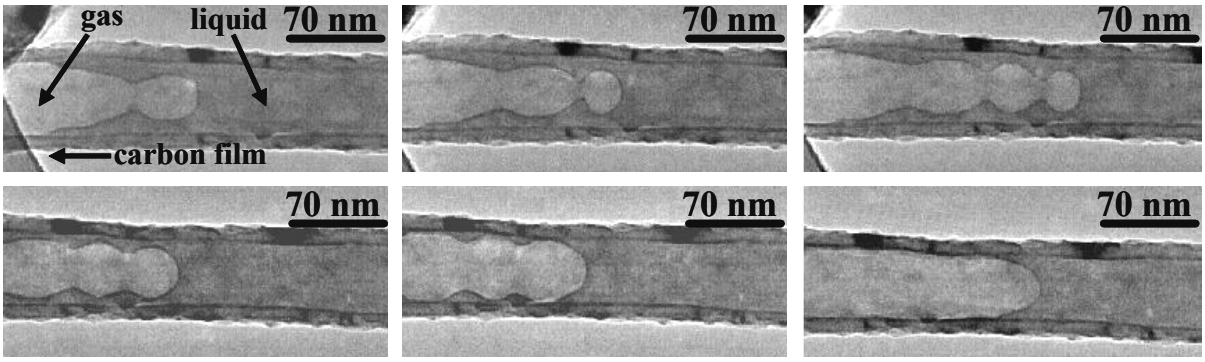

Fig. 2: Time sequence of TEM images displaying liquid/gas interface propagation in a closed hydrothermal CNP subjected to sustained constant heating via electron irradiation. A complex interface forms, then moves from left to right via repeated bubble formation in the adjoining bulk liquid. The wave-like pattern on the inner wall is an outcome of the pinched-off liquid between neighboring bubbles. This entire sequence lasted for about one minute.

2. Nanotube-Based Nanofluidic Devices

Our device[6] (Fig. 3), was fabricated through a combination of standard microfabrication processes and dielectrophoretic trapping of individual carbon nanotubes. The CNPs were assembled between the two trapping electrodes using dielectrophoresis. In the experiments, we applied a 12 V_{pp} potential at 2 MHz between a pair of electrodes. The CNP solution was exposed to the electric field for about 30 seconds. Fig. 4 depicts the positioning of the CNP during the trapping process. When the CNP was far from the trap, it moved towards the 8-μm gap at a nearly level height above the electrodes and with a nearly uniform speed, while rotating so as to align itself with the electric field. Once arriving in the vicinity of the gap, the CNP's trajectory underwent an abrupt turn, and it accelerated towards the electrode gap. This rapid acceleration corresponded to the intensifying electric field gradient that the particle encountered while approaching the trapping site. At the conclusion of the trapping process, individual CNPs were trapped in the gap between two adjacent electrodes with each of their ends resting on a different electrode (Fig. 5).

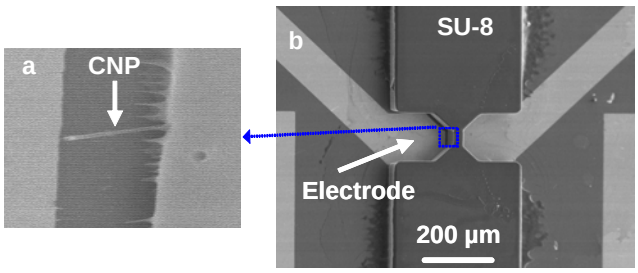

Fig. 3: SEM images of the nanotube-based fluidic device. SU-8 photoresist spun over a substrate with trapped nanotubes was developed to form fluidic interconnects.

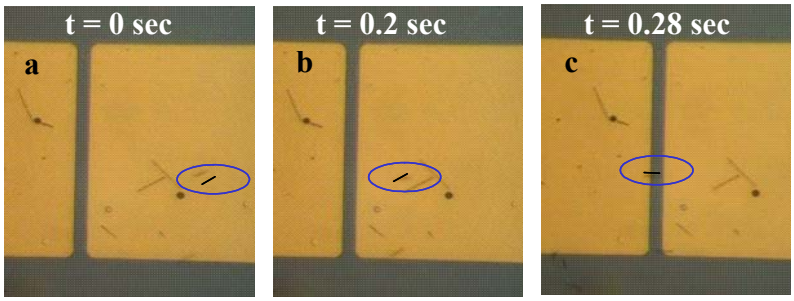

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Fig. 4: Images of the CNP during various stages of the trapping process. The CNP is encircled with for better visibility.

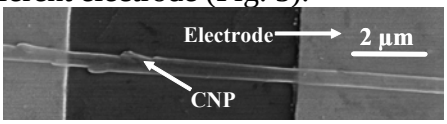

Fig. 5: SEM image of a trapped tube in the gap between a pair of electrodes.

3. Contactless Nano-Syringe

It is important to be able to direct fluids to CNP probes. Water can be selectively directed toward certain locations or injected into the tip of an isolated CNP using hydrophilic polypyrrole guides[7]. The polypyrrole was positioned onto one tip of the nanotube by the application of an external electric field leading to highly localized bipolar (contactless) electrodeposition (Fig. 6).

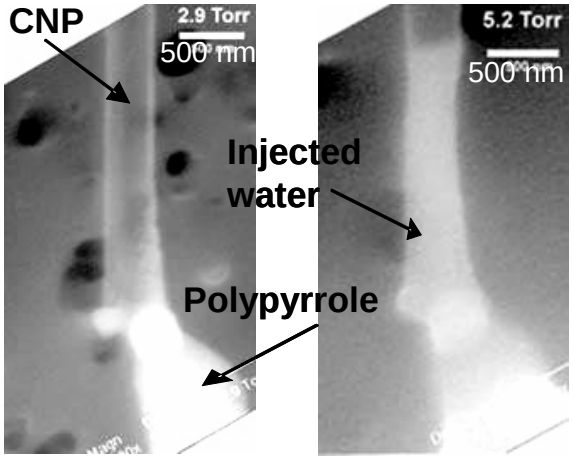

Fig. 6: ESEM images showing the condensation of water from the polypyrrole deposit into the CNP.

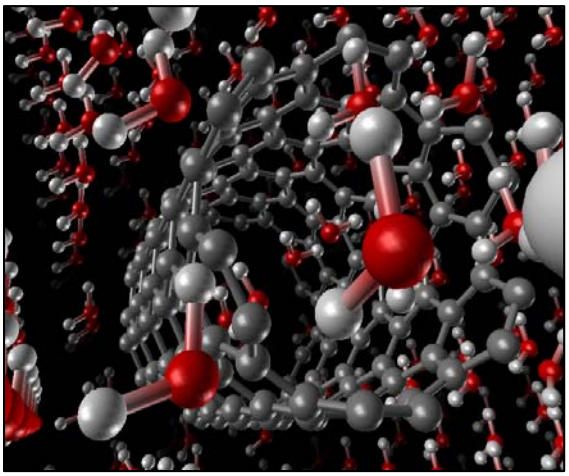

Fig. 7: Simulation of transport of water molecules through a carbon nanotubes (no wetting).

4. Computational Nanoscale Hydrodynamics

We also investigate computationally the hydrodynamics of purified and doped carbon nanotubes in aqueous and ionic environments (http://www.icos.ethz.ch). Computations based on molecular dynamics and multiscale computational techniques have shown the non-wetting wetting behavior of small-diameter (1-5 nm) CNT, which was confirmed experimentally by *in-situ* TEM. Suitable molecular dynamics potentials have been developed based on experimental results and quantum mechanics calculations.[8] Wetting of modified graphitic surfaces by nanoscale droplets is, as manifested by the contact angle, dependent on the doping of the graphitic surface and the presence of ions in the droplet. Ongoing investigations involve the transport of water molecules through doped and purified carbon nanotubes (Fig. 7).

Field of Impact

This research program has visualized multiphase fluid motion in real time at length scales approaching molecular dimensions. We are developing new assembly and fabrication techniques for the manufacturing of nanofluidic systems. The project is likely to contribute to fundamental physics by providing information on the behavior of liquids under extreme confinement. Additionally, the project is likely to contribute to the fields of biology, medicine, and homeland security by facilitating the development of nanoscale biosensors and cellular probes.

References

1. Gogotsi, Y., Libera, J. & Yoshimura, M. Hydrothermal Synthesis of Multiwall Carbon Nanotubes. *J. Mater. Res.* **15**, 2591-2594 (2000).
2. Megaridis, C. M., Guvenc-Yazicioglu, A., Libera, J. A. & Gogotsi, Y. Attoliter fluid experiments in individual closed-end carbon nanotubes: liquid film and fluid interface dynamics. *Phys. Fluids* **14**, L5-L8 (2002).
3. Gogotsi, Y., Libera, J. A., Güvenç-Yazicioglu, A. & Megaridis, C. M. *In-situ* Multi-phase Fluid Experiments in Hydrothermal Carbon Nanotubes. *Applied Physics Letters* **79**, 1021-1023 (2001).
4. Ye, H., Naguib, N., Gogotsi, Y., Yazicioglu, A. G. & Megaridis, C. M. Wall Structure and Surface Chemistry of Hydrothermal Carbon Nanofibers. *Nanotechnology* **15**, 232-236 (2004).
5. Gogotsi, Y., Naguib, N. & Libera, J. A. In situ Chemical Experiments in Carbon Nanotubes. *Chemical Physics Letters* **365**, 354-360 (2002).
6. Riegelman, M., Liu, H., Evoy, S. & Bau, H. H. in *Proceedings of NATO-ASI: Nanoengineered Nanofibrous Materials* (Antalya, Turkey, 2003) Eds. S. Guceri, V.L. Kuznetsov, Y. Gogotsi, Kluwer, 2004
7. Bradley, J.-C., Ndungu, P., Babu, S., Tromp, J. & Hackett, N. Bipolar electrodeposition of polypyrrole onto carbon nanotubes. *CPS: chemistry/0308001* (2003).
8. Werder, T., Walter, J. H., Jaffe, R. L., Halicioglu, T. & Koumoutsakos, P. On the Water - Carbon Interactions for Use in Molecular Dynamics Simulations of Graphite and Carbon Nanotubes. *J. Phys. Chem. B* **107**, 1345-1352 (2003).

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