In situ Fluid Studies in Carbon Nanotubes with Diameters Ranging from 1 to 500 nm

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Abstract: - 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, 1-50 nm inner diameter) and nanopipes (CNP, 50-300 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 surface chemistry on liquid behavior in carbon nanotubes. 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 and CNT have been examined. Fluid behavior and chemical modification of the tubes have been investigated. This paper will give an overview of experimental studies of behavior of aqueous fluids in carbon nanotubes.

Key-Words: - Carbon nanotube, nanofluidics, fluid transport, wetting, contact angle, surface chemistry

1 Introduction

Nanofluidic research has increasingly expanded in the last few years from the early work based on molecular dynamics simulations to experimental measurements of fluid velocity in multi-walled carbon nanotubes (MWNT) [1]. Initial numerical predictions proved to be contradicting, with indications that water would not fill carbon nanotubes based on the non-wetting behavior of graphite [2], and, on the other hand, suggestions that water molecules would form single or double helical strands [3] or even pearl-like chains [4] in single-walled carbon nanotubes (SWNT) due to the confinement effect. Numerical models also showed that water molecules at ambient pressure and room temperature should transition to a quasi-solid phase as an effect of confinement forming complex ice-like structures inside SWNTs and MWNTs [5,6].

The first direct observation of water in a hydrothermally synthesized carbon nanotube showed water forming a low contact angle, wetting meniscus [7]. More recently, fluid flow measurements in 2 and 7 nm diameter carbon nanotubes have shown fluid velocities up to 105 times faster than what predicted by classical fluid dynamics calculations [8,9]. It is still unclear, though, if this unusual behavior is caused by space confinement, the structure or chemistry of the nanotube walls, or all of the above.

In this paper we review experimental observations of fluids in carbon nanotubes with diameters ranging from 1 to 500 nm with particular attention on the effect of the nanotubes' surface chemistry and structure on their interaction with the investigated fluids.

2 Fluid Studies in Multi-Walled Nanotubes (1 – 100 nm)

Transmission electron microscopy (TEM) was used to study the behavior of water trapped in closed nanotubes with diameters from 1 to 100 nm.

2.1 SWNTs

We have visualized fluid motion in real time at length scales approaching molecular dimensions. TEM micrographs of SWNTs and double-walled carbon nanotubes (DWCNT) hydrothermally filled with water show chains of water molecules forming a double-helix structure along the nanotubes' axis (Figs. 1a and 1b). A very slow liquid dynamics has been observed at this length scale, as demonstrated by the possibility of in-situ TEM observation and image recording. This suggests an ice-like behavior of water. In slightly larger nanotubes of 3-6 nm in diameter (Fig. 1c), a clear interface between the liquid and vapor phases cannot be detected. This suggests that we are under the threshold below which classical continuum fluid mechanics cannot

be used anymore. A transition to the continuous meniscus was observed at the inner tube diameter of about 10 nm.

2.2 Hydrothermal MWNTs

Hydrothermal nanotubes were synthesized using a carbon precursor and water in a high pressure – high temperature autoclave. As a result, capped MWNTs were formed, filled with high pressure fluids in the liquid and vapor phase (Fig. 1d). The graphitic structure of the hydrothermal MWNT is able to withstand the difference in pressure between the fluid in its inside and the ultra high vacuum of the TEM column. By focusing the electron beam on the liquid phase, liquid evaporation and condensation can be induced with the formation of vapor bubbles [7]. The low contact angle of the water phase wetting the tube's internal wall is due to the presence of oxygen-based terminations on the inner walls of the tubes, as a result of the hydrothermal synthesis [7,10,11].

3 Fluid Studies in Large MWNTs and Nanopipes

The environmental scanning electron microscope (ESEM) is a powerful tool for *in situ* analysis of the wetting of CNT with water. The ability of the ESEM to condense and vaporize liquids within the chamber has enabled the dynamic study of CNT/water interactions, including condensation, transport and evaporation of water and other liquids inside open tubes [12]. CNT with inner diameters from 10 to 300 nm have been fabricated by chemical vapor deposition (CVD) from ethylene gas in an Al_2O_3 membrane [13]. When studying the interaction of these CNT with water, it was possible to see liquid menisci inside the CNT [12]. From the small measured contact angles, it is clear that these CNTs are hydrophilic. Complex meniscus shape and slow liquid dynamics due to water confinement have been observed [14]. It is possible to control the contact angle that water forms inside the CVD nanotubes by controlling the surface chemistry and structure of the carbon nanotubes [13,15]. In the wetting condition (Fig. 1e) water fills the nanotube forming a low contact angle meniscus. In the non-wetting condition (Fig. 1f) water does not enter the hydrophobic nanotubes, but forms high contact angle drops on its surface.

4 Conclusions and Future Perspectives

In this brief review we have shown that it is possible to fill carbon nanotubes having diameters from 1 to 500 nm with water using different techniques. The diameter, surface structure and chemistry of the nanotubes all affect the nanotube-water interactions, giving the possibility of controlling it, and hence ultimately controlling the liquid flow through the tube. Currently we are developing multifunctional nanotubes [16] and use them to fabricate CNT-based pipettes for nano- and attofluidic applications such as sub-cellular interrogation and probing [17].

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References

[1] Whitby, M.; Quirke, N. Nature Nanotechnology, 2, 2007, pp. 87.
[2] Werder, T.; Walther, J. H.; Jaffe, R. L.; Halicioglu, T.; Noca, F.; Koumoutsakos, P. Nano Letters, 1, 12, 2001, pp. 697.
[3] Kotsalis, E. M.; Walther, J. H.; Koumoutsakos, P. International Journal of Multiphase Flow, 30, 2004, pp. 995.
[4] Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. Nature, 414, 2001, pp. 188.
[5] Koga, K.; Gao, G. T.; Tanaka, H.; Zeng, X. C. Nature, 412, 2001, pp. 802.
[6] Noon, W. H.; Ausman, K. D.; Smalley, R. E.; Ma, J. Chemical Physics Letters, 355, 2002, pp. 445.
[7] Gogotsi, Y.; Libera, J. A.; Yazicioglu, A. G.; Megaridis, C. M. Applied Physics Letters, 79, 7, 2001, pp. 1021.
[8] Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. Science, 312, 5776, 2006, pp. 1034.
[9] Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. Nature, 438, 7064, 2005, pp. 44.
[10] Gogotsi, Y.; Naguib, N.; Libera, J. A. Chemical Physics Letters, 365, 3-4, 2002, pp. 354.
[11] Ye, H.; Naguib, N.; Gogotsi, Y.; Yazicioglu, A. G.; Megaridis, C. M. Nanotechnology, 15, 2004, pp. 232.
[12] Rossi, M. P.; Ye, H.; Gogotsi, Y.; Babu, S.; Ndungu, P.; Bradley, J. C. Nano Letters, 4, 5, 2004, pp. 989.
[13] Mattia, D.; Bau, H. H.; Gogotsi, Y. Langmuir, 22, 4, 2006, pp. 1789
[14] Yarin, A. L.; Yazicioglu, A. G.; Megaridis, C. M.; Rossi, M. P.; Gogotsi, Y. Journal of Applied Physics, 97, 2005, pp. 124309.
[15] Mattia, D.; Rossi, M. P.; Kim, B. M.; Korneva, G.; Bau, H. H.; Gogotsi, Y. Journal of Physical Chemistry B, 110, 20, 2006, pp. 9850
[16] Mattia, D.; Korneva, G.; Sabur, A.; Friedman, G.; Gogotsi, Y. Nanotechnology, 18, 2007, pp. 155305
[17] Freedman, J. R.; Mattia, D.; Korneva, G.; Gogotsi, Y.; Friedman, G.; Fontecchio, A. K. Applied Physics Letters, 90, 2007, pp. 103108

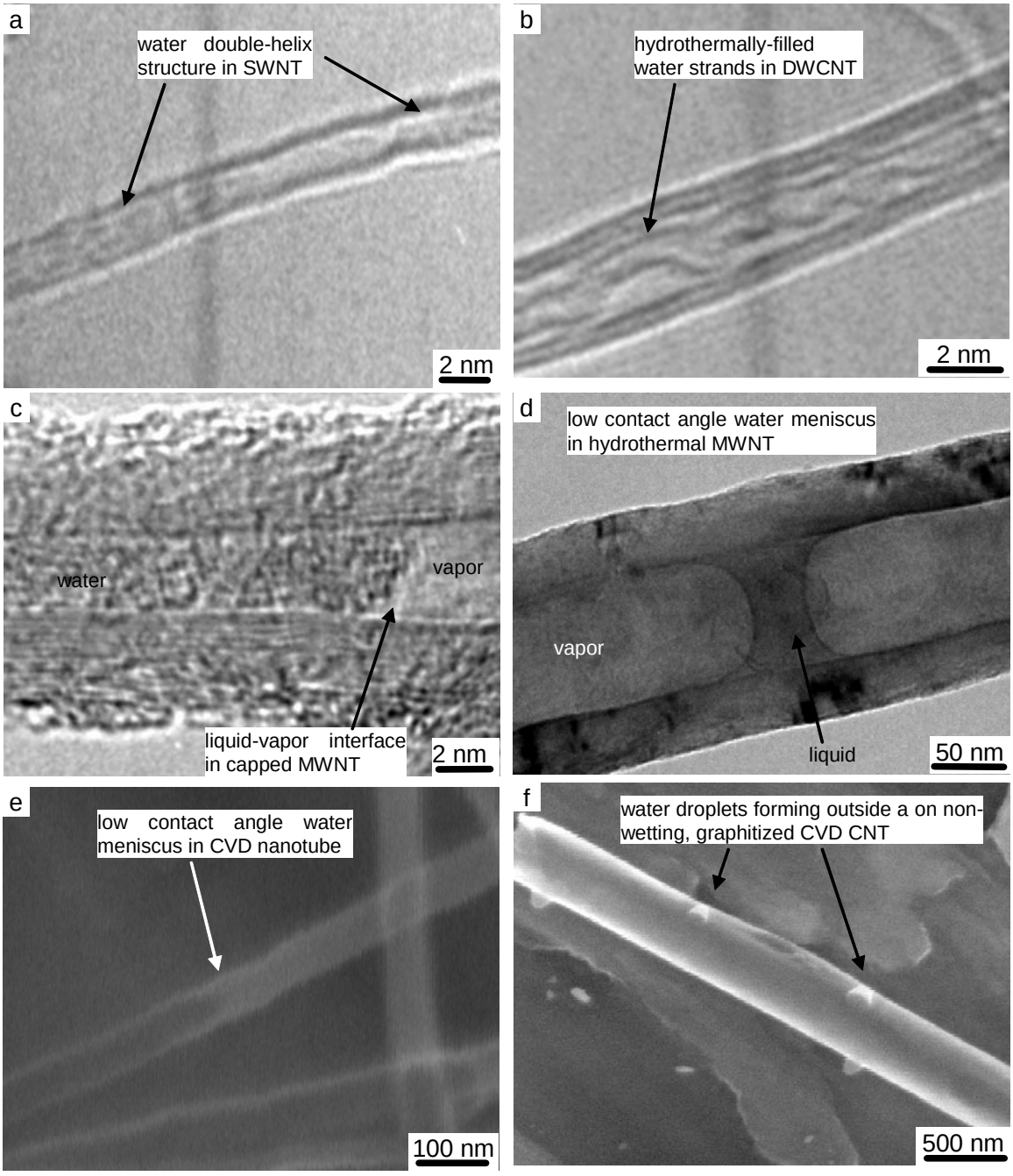

Figure 1. TEM and SEM images of water inside carbon nanotubes and nanopipes:
a,b) TEM micrographs of double–helix water strands in (a) SWNT and (b) DWNT. c) TEM micrograph of the interface between water molecules and vapor in a capped MWNT. d) TEM micrograph of a low contact angle liquid meniscus between 2 vapor bubbles in a hydrothermal MWNT. e) Water-filled CVD MWNT in the environmental SEM.
f) Water droplets forming outside a graphitized CVD nanotube in the environmental SEM.