Observation of Water Confined in Nanometer Channels of Closed Carbon Nanotubes

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ABSTRACT

We present a method to fill 2−5-nm-diameter channels of closed multiwalled carbon nanotubes (MWNT) with an aqueous fluid and perform in situ high-resolution observations of fluid dynamic behavior in this confined system. Transmission electron microscope (TEM) observations confirm the successful filling of two types of MWNTs and reveal disordered gas/liquid interfaces contrasting the smooth curved menisci visualized previously in MWNT with diameter above 10 nm. Electron energy loss spectroscopy (EELS) and energy dispersive spectrometry (EDS) analyses, along with TEM simulation, indicate the presence of water in MWNT. A wet−dry transition on the nanometer scale is also demonstrated by means of external heating. The results suggest that when ultrathin channels such as carbon nanotubes contain water, fluid mobility is greatly retarded compared to that on the macroscale. The present findings pose new challenges for modeling and device development work in this area.

Water confined in nanoscale channels is of great interest in biology, geology, and materials science. An excellent model for observing such behavior is water entrapped inside carbon nanotubes. To utilize carbon nanotubes in nanofluidic applications such as nanofluidic chips, cellular probes, and capsules for drug delivery, a fundamental understanding of water behavior inside the tubes must be established first. As a consequence, water behavior in confined systems, and more specifically in carbon nanotubes, is currently the subject of intense scrutiny. Such behavior has been thoroughly studied theoretically4−6 as well as by using indirect observations through neutron scattering techniques7 and X-ray diffraction,8 which showed the crystallization of water confined inside single-walled nanotubes (SWNT). So far, aqueous fluids in 50−100-nm-diameter nanotubes have been observed using TEM,9−12 but no direct observations of water in an extremely confined space corresponding to 10 molecular layers or less have been reported yet.

Even in the case of simple fluids (small neutral molecules), it has been reported that nanoscale confinement may cause some phase transitions that cannot occur on the macroscale.13 It has been shown by molecular dynamics simulations that in confined systems, such as nanotubes, when a fluid is entrapped, its phase behavior is altered and some excluded volume effects become apparent.14 Some examples of sub-attoliter systems studied experimentally are cyclohexane confined between mica layers,14,15 metals, gases,16,17 molten salts, halides, oxides, and fullerenes inside nanotubes. (See ref 18 for a review.) In the case of water, the polar nature of its molecules combined with its relatively high surface tension present additional challenges, as compared to simple fluids.

In the molecular dynamics modeling community, the debate of how water flows in nanochannels still continues.19−21 Drying transitions may occur on the nanoscale as a result of strong hydrogen bonding between water molecules, which can cause the liquid to recede from nonpolar surfaces and form distinct layers separating the bulk from the surface.22 The study of water on hydrophobic surfaces suggests the presence of weak hydrogen bonding23 or even the destruction of hydrogen bonding in very narrow tubes,24 whereas other studies suggest that significant water occupancy exists inside the tubes despite the reduced number of hydrogen bonds compared to the number in the bulk fluid.4 New phases of
ice inside carbon nanotubes have been predicted, but not all scientists agree that these ice phases can indeed exist. It has also been shown by molecular dynamics that \( \text{OH}^- \) bonds involved in hydrogen bonds are almost aligned along the carbon nanotube axis and that water molecules may rotate freely around their aligned hydrogen bonds. The fluidity of water has also been discussed either by stating that water viscosity remains close to its bulk value or that the flow appears to be frictionless, being limited only to the barriers of entry, and finally that the number of hydrogen bonds decreases at the interfacial regions. It has further been shown that a water molecule spends a longer time in its neighborhood in smaller tubes rather than in larger tubes and, as expected, in bulk water. A new study of aqueous liquid–vapor interfaces has been reported recently, but to date, no experimental observation has confirmed or disputed the proposed models. In the present study, we have filled thin, hollow channels of closed nanotubes with H\(_2\)O and D\(_2\)O (heavy water). Using TEM and EELS analysis, we have carefully examined the water behavior in this confined system.

Initially, hollow, closed nanotubes with an inner diameter in the range 2 to 5 nm (Figure 1A) were filled with water (Figure 1B) by autoclave treatment at different temperatures and pressures. To confirm that the material inside the tube was water and not amorphous carbon or hydrocarbons trapped during synthesis, EELS analysis of the nanotubes, before and after filling, including spectral imaging in scanning transmission electron microscopy (STEM) mode, was performed. Previous EELS work conducted on crystalline ice demonstrated that the corresponding spectra have a characteristic peak in the low-loss region (9.1 eV), which corresponds to water molecule excitation. When we filled nanotubes produced by chemical vapor deposition (CVD) with water and cooled them down to \(-80 \, ^\circ\text{C}\), an EELS peak at the same position was recorded (spectrum a in Figure 2A), confirming the presence of ice. For comparison, EELS spectra of an empty nanotube (spectrum b) and a supporting carbon film (spectrum c) were also recorded. They did not show the characteristic peak of ice. The first high-energy plasmon peak at 22.8 eV of MWNT with ice is consistent with that of the empty MWNT, as indicated by the first dashed line in Figure 2A. The second plasmon peak at 27.3 eV can be attributed to the supporting carbon film, as
indicated by the second dashed line, because the investigated MWNT with ice was supported on the carbon film. Because the sample was observed in the high-vacuum region (1.5 \times 10^{-5} \text{ Pa}) of the TEM for a prolonged time before cooling, no water adsorbed on the outer surface of the nanotubes could be sustained. Therefore, the peak at 9.1 eV in Figure 2A may originate only from the ice entrapped inside the nanotube channels. The present peak at 9.1 eV is more blunt than the one reported in ref 33, probably because of the scattering effect of carbon surrounding the ice and confinement inside a nanometer channel. A typical EELS spectrum acquired from room-temperature nanotubes is shown in Figure 2B. The features at 284 and 532 eV correspond to the carbon K-edge and oxygen K-edge, respectively. The \( \pi^* \) peak of the carbon K-edge reveals the sp\(^2\)-type bonding in the graphitelike tube walls of the MWNT. Because STEM has a precise 1-nm-diameter electron-beam probe, the oxygen edge detected from the center of a carefully selected nanotube can be attributed only to water inside or oxygen-containing functional groups attached to the nanotube walls, not catalysts or impurities. Combining the EELS results in Figure 2A and B, we infer that the investigated nanotubes have water entrapped in their channels. The EELS spectrum images (Figure 2D – carbon map, Figure 2E – oxygen map; both have 5-nm pixels) were obtained from the cluster of filled carbon nanotubes shown in Figure 2C. The “null element” map (at 110 eV) was checked in advance, and no significant artifacts due to systematic errors in the background were present. The contrast change in the carbon map (Figure 2D) reflects a change in the quantity of carbon nanotubes. It is clearly visible in the oxygen map (Figure 2E) that oxygen atoms form chains of white spots corresponding to water molecules aligned within carbon nanotubes arranged in bundles. However, the distribution of water in nanotubes is far from homogeneous. EDS analysis of nanotubes produced by CVD and arc evaporation (AE) was also performed before and after hydrothermal treatment (Figure S1). For both types of nanotubes, there is no oxygen signal from the as-received samples, as expected (Figure S1A). However, for the filled CVD tubes, there is a very strong oxygen signal (Figure S1B).
compared to the oxygen signal obtained from the treated AE tubes (Figure S1C). The lower oxygen signal of the AE tubes is due to the fact that a smaller percentage of AE tubes were filled with water. AE tubes have well-ordered walls, which are more difficult for water molecules to penetrate during autoclave treatment. Furthermore, AE tubes did not contain catalysts (as confirmed by EDS spectra), thus the detected oxygen could not originate from oxidized catalyst particles. The oxygen signal from both types of tubes after autoclave treatment provides further evidence that water is entrapped inside the tubes. It is worth noting that the EDS and EELS results do not eliminate the possibility of presence of some amorphous carbon or C—O—H species inside the nanotubes. However, the apparent mobility of the fluid inside the tube and its disappearance upon sustained heating (evaporation) reduce the possibility that this phase might be amorphous carbon. To eliminate the possibility of C—O—H species, we used Fourier transform infrared spectroscopy (FTIR) analysis on tubes filled with H2O and D2O. No intense peaks of organic species were recorded. D2O was detected using FTIR. This provides independent confirmation of water trapped in the tubes after autoclave treatment. Although H2O may be adsorbed from air, D2O may be present inside the tube only after autoclave treatment and drying. Finally, because purified CVD MWNT and pure water were used in the autoclave treatment and the lowest-treatment temperature (300 °C) was well below the reaction temperature of graphite and water, the fluid inside the MWNT must be water. Liquid water and well-defined menisci (Figure S2) were clearly observed in larger-diameter (20–100 nm) MWNT treated in autoclaves under the same conditions.11,12

After hydrothermal treatment, many of the nanotubes were confirmed to be partially filled with the aqueous fluid (Figures 1B and 3A). This segmented filling could be explained as follows: during autoclave treatment, supercritical water penetrates through wall defects (when present) and occupies the whole volume of the nanotube channel. During the cooling stage, the temperature of the nanotube contents decreases along with the pressure (closed system), eventually causing water condensation and the appearance of gas/liquid interfaces.9 In small-diameter nanotubes (Figure 1B), there is no clear meniscus separating the gas and the liquid, unlike the situation in larger tubes (20–100 nm, Figure S2), where water appears to occupy volumes having shapes consistent with macroscopic behavior.11,12 This important difference suggests that for length scales of 5 nm or less, water molecules at the liquid/gas interface may no longer exhibit bulklike behavior seen in larger-diameter tubes. The random movement of water molecules and vibration at the liquid/gas interface can apparently overcome the restraint of surface tension and cause the formation of disordered interfaces. Figure S2 shows distinct water volumes in different types of MWNT with different diameters. Both large hydrothermal MWNT with an inner diameter of 50 nm (Figure S2A) and ~10-nm AE MWNT (Figures S2B and S2C) show distinct water/gas interfaces (menisci). Therefore, in comparison to smaller-diameter nanotubes (Figures 1B and 3A), it might be concluded that the transition from continuum to molecular behavior (as far as the appearance of gas/liquid interfaces is concerned) occurs somewhere between 5 and 10 nm in diameter.

The fluid volume shape seen in Figure 1B is in agreement with the published model of a water droplet in a 5-nm carbon nanotube.20 The structural HyperChem simulation (Figure 1C) conducted for water in a (30, 30) carbon nanotube of 4.07-nm diameter shows a random distribution of water molecules in the nanotube channel, which is in agreement with that observed in Figure 1B. Figure 1D shows two multislice TEM simulations produced for water molecules inside a (30, 30) carbon nanotube and without any nanotube surrounding them, respectively. The focal series images correspond to different defocus Z values from 10 to 90 nm, with an increment of ΔZ = 20 nm. This simulation confirms that the water molecules are able to produce a strong contrast in the high-resolution TEM images when the focal conditions are appropriate, despite their small molecular size and random distribution. Optimum adaptation of simulated images (Figure 1D) to the experimental TEM image (Figure 1B) is achieved for a defocus setting of 50 nm. It is worth noting that the black dots in the simulated TEM image for water, such as that indicated by an arrow, often correspond to a cluster of water molecules (as indicated by a circle in the model structure) rather than a single water molecule. Better TEM conditions are required to resolve single molecules in a cluster.

The filling efficiency of MWNT with water, as determined by the TEM observation of a large number of CVD tubes, increases with temperature and pressure, as shown in Figure S3. At 80 MPa and 300 °C, only 4% of all nanotubes were filled (Figure S3A), whereas only 10% of nanotubes were filled at 50 MPa and 650 °C (Figure S3B). Fifteen percent of all nanotubes were filled at 80 MPa and 650 °C. The latter condition is considered to be optimum for filling because at temperatures higher than 700 °C chemical reactions between graphite and water are expected to occur.12 Figure S3 is consistent with the hypothesis that once the water critical point (374.14 °C, 22.064 MPa) is exceeded water penetrates much more easily through defects in the thin tube walls because the hydrogen bonds between molecules are weakened and hydrogen bond networks break.30

Using the present water-filled MWNT, the dynamic response of liquid—gas interfaces can be investigated by focusing the TEM beam on segments of the tube where entrapped water is visible. Beam heating has been shown to cause the effective evaporation of water in large tubes with 100 nm diameter.9,11,34 Figure 3 demonstrates how electron bombardment affects water behavior in CVD MWNT. Beam heating causes the water droplet in Figure 3A to undergo an apparent volume rearrangement/expansion (Figure 3B). Molecular dynamics simulation by HyperChem (Figure 3C at room temperature and Figure 3D at 75 °C) corroborates such an expansion. At the same time, electron bombardment causes a disordering of the nanotube walls and may also be partially responsible for spreading the water droplet in Figure 3B. Figure 3E shows that focusing the electron beam may lead to nanobubble formation in the fluid (shown by
the black arrow). This could be attributed to either evaporation or radiolysis of the liquid. Our earlier work (see refs 9 and 11) on 50–100-nm-diameter nanotubes has provided direct evidence of reversible phenomena caused by gentle electron beam irradiation. Given that radiolysis is an irreversible process, heating seems to precede radiolysis. In the same publications,9,11 we also reported irreversible phenomena that occur only under intense irradiation and could be caused by radiolysis or chemical interactions between the fluid and tube walls. Thus, it is plausible that the bubbling seen in Figure 3E could be caused by radiolysis, but the effect of heating is expected to dominate. The voids increase as electron bombardment continues in Figure 3F. The time interval between the events shown in Figure 3A and B is several seconds. The corresponding time between the events shown in Figure 3E and F is about 1 min. Given the fine length scales \( L \) of these water volumes \( (L \approx 10–100 \text{ nm}) \) and considering typical values of self-diffusion of bulk liquid water at atmospheric pressure \( (D \approx 10^{-9} \text{ m}^2/\text{s}) \), one would expect such processes to occur over characteristic times of \( L^2/D \), or several microseconds. To this end, the characteristic times for the phenomena observed in Figure 3 are several orders of magnitude longer than expected on the basis of macroscopic transport properties of water. This contradicts the prediction that confined water retains its bulk fluidity.5 The observed slow response of water could be due to the known presence of hydroxyl groups10 on the inner tube walls. Water molecules could be pinned to these hydroxyl groups forming strong hydrogen bonds, which may influence any bulklike behavior.36 In addition, van der Waals forces between tube walls and water molecules (Figure 3B) may play an important role in decreasing the mobility of

**Figure 3.** Dynamics of water heated in CVD MWNT. (A) TEM image of MWNT with entrapped water. (B) Spreading of water due to electron beam heating and deformation of nanotube walls due to electron bombardment. (C and D) HyperChem simulation of images A and B, respectively. The temperature is 25 °C for C and 75 °C for D. From E to F, a nanobubble (indicated by arrow) is transformed to two nanobubbles under electron beam heating.
water. Finally, increased water viscosity in confined spaces\(^{27}\) may also be responsible, at least in part, for the observed behavior.

The observed MWNT show hydrophobic behavior, as shown in Figure 3A, E, F and Figure 4, where gaps and bubbles are present between tube walls and the fluid. For a graphene sheet, no wetting is expected.\(^{26}\) However, in some cases (Figure 1B), these gaps between the fluid and the walls are absent, possibly because of surface defects that contain dangling bonds that may trigger strong chemical interactions with water molecules. In other cases, as in Figure 3B, thermal stimulation seems to affect the wetting behavior.

Water trapped in more ordered AE nanotubes shows behavior similar to that in CVD nanotubes. In addition, this behavior does not depend on the number of graphene layers in the wall (Figure 4A and B). Filling experiments of CVD MWNT with heavy water (D\(_2\)O) produced similar results to those with regular water (Figure 4C). Figure 4C confirms that D\(_2\)O does not wet the inner tube wall surface, as demonstrated by the clear separation (white arrow) between the walls and the entrapped liquid. It is expected that during autoclave treatment water penetrates the nanotube shell through defects in the walls, as shown by the dark arrow in Figure 4C. The escape of water through a similar defect was observed upon electron beam heating of a larger nanotube filled with water.

AE nanotubes have fewer defects than CVD tubes, which makes them more difficult to fill with water, as shown by the low oxygen EDS signal in Figure S1C. In general, defect-free tubes may be difficult to fill because most MWNT are closed by catalyst particles or carbon domes at both ends. Open-ended tubes are not able to hold the liquid in the vacuum of the TEM column and consequently lose water prior to observation. Defects act as a valve that opens under high pressure and temperature and allows supercritical water to flow into the nanotube chambers. The same defects close up during autoclave cooldown, thus preventing water from escaping from the CNT interior when the system is depressurized. These valves can be opened again by heating the tube with an electron beam or by using other energetic means that allow for the controlled or even explosive release of the fluid contents from the nanotube.

Anchoring of aqueous fluid and the slow response to thermal stimuli in thin tubes suggest obstacles in the transport of large volumes of liquids through nanofluidic devices implementing nanotubes or nanopipes. Thus, perfect tubes with no wall defects may be required for the efficient transport of aqueous liquids through nanometer channels.
which might not be practically feasible. On the other hand, fluid release with molecular-level control may be achievable using these systems.

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Supporting Information Available: Description of materials and methods. Figures S1, S2, and S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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