In situ chemical experiments in carbon nanotubes

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Received 6 May 2002; in final form 20 August 2002

Abstract

Understanding the interaction of water-based liquids with carbon at the nanoscale is very important for exploring the potential of carbon nanotubes in nanofluidic chips, probes, and capsules for drug delivery. By using hydrothermal synthesis, we produced closed hydrophilic multiwall carbon nanotubes filled with aqueous fluid. They allow for the first time high-resolution in situ studies of an interface between fluid and carbon in TEM. Strong interaction between the liquid and walls, intercalation of nanotubes with O–H species and dissolution of walls upon heating have been demonstrated. Thermodynamics simulation was used to explain the interaction of nanotubes with fluid.

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1. Introduction

Novel carbon-based materials and structures are seen today as key in the implementation of nanotechnology. Carbon nanotubes are among the most exciting new materials being investigated and synthesized because of their potential for use in new technologies and devices. In particular, multiwall carbon nanotubes are of interest to the growing micro- and nanofluidic industry, which is a new branch of microengineering with great promise [1]. However, simulation of water in nanotubes predicts non-wetting behavior at room temperature [2,3], which is in agreement with the hydrophobic behavior of graphite surfaces [4].

This can limit the use of carbon nanotubes for transport of aqueous fluids. Experimental in situ studies are required to understand the interactions between the water-based fluid and the tube walls.

Most of previous work on the interactions between solids and water in thin films was done on clays and zeolites [5,6]. Since these materials lose water easily in a vacuum, no in situ TEM observations could be made. NMR or neutron diffraction [6] were used to supply data for modeling water–surface interactions [7]. The same approach was used to study intercalation of graphite [8]. Therefore, the amount of experimental data is scarce and the theoretical studies did not receive sufficient experimental verification. Lattice resolution studies of liquid–solid interfaces in TEM have been limited to a few exotic systems such as metals or liquid inert gases [9]. No high-resolution studies of carbon–water interface have ever been reported. Closed carbon nanotubes provide a...
unique opportunity for in situ TEM study of the chemical interactions between aqueous fluids and carbon.

Visualization of the behavior of aqueous liquids on nanoscale have been only recently achieved due to use of hydrothermal nanotubes containing encapsulated water and gases [10,11]. Multiwall carbon tubes with internal diameters from 50 to 100 nm have been used as a test platform for in situ fluid dynamics experiments in a transmission electron microscope (TEM) [12–14]. Wetting, evaporation, condensation and expansion phenomena have been monitored in TEM and reported in our previous publications [12–14].

This Letter reports results of in situ chemical experiments using the aqueous fluid trapped in hydrothermal carbon nanotubes. The objective of the study was to conduct analysis of the fluid composition in the nanotubes and investigate interaction between the fluid and carbon walls. Equilibrium thermodynamics was used to support experimental TEM studies.

2. Experimental

Graphitic carbon nanotubes were synthesized hydrothermally by using an ethylene glycol (C$_2$H$_4$O$_2$) solution in the presence of a Ni catalyst at 730–800 °C under 60–100 MPa pressure as described in [10,11,15]. TEM analysis shows that these carbon nanotubes are characterized by having high perfection of graphene layers, long and wide internal channels and Ni inclusions in the tips. Typically, hydrothermal nanotubes have 20–70 fringes in the wall (wall thickness 7–25 nm) and outer diameter of 50–150 nm. Thin-wall carbon tubes with internal diameters from 10–1000 nm have been produced [15]. Most of the tubes are hollow from tip to tail, a few show internal closures; most closed and some open. During growth of a tube, the synthesis fluid, which is a supercritical mixture of CO, CO$_2$, H$_2$O, H$_2$, and CH$_4$ [16], enters the tube. After closure of the tube and temperature decrease, aqueous liquid and gases are trapped inside. Therefore, closed hydrothermal nanotubes, unlike conventional nanotubes produced in vacuum or at ambient pressure [17], contain water and gases encapsulated under pressure. These liquid inclusions were studied by using TEM, where apparent condensation and evaporation of liquid can be observed in situ. TEM analysis was performed using a JEOL JEM-3010 (300 kV) with a lattice resolution of 0.14 nm and a field-emission STEM JEOL 2010F (200 kV) with a lattice resolution of 0.1 nm. The microscopes were equipped with an energy dispersive spectrometer (EDS) with a light element X-ray detector analyzer. TEM samples were prepared by dispersing nanotubes in acetone or isopropanol and placing drops onto lacey carbon grids. TEM provides the capability of studying the interaction between the enclosed liquid and the tube walls with close to 0.1 nm resolution. ChemSage 4.14 advanced Gibbs energy minimization program from GTT, Germany, was used to model the interaction between carbon and hydrothermal fluids. Closed systems and ideal gases, with liquid water excluded from calculations, were assumed as in previous studies of hydrothermal systems [16].

3. Results and discussion

Fig. 1 shows typical hydrothermal nanotubes, which have a large internal diameter, nanoscale graphitic walls of 10–30 nm with minimal disorder and a high continuity of graphene planes. The capped tubes are gas-tight and can maintain high internal pressure in the vacuum (10$^{-8}$ torr) of a TEM, thus, demonstrating very high containment strength. Some of the closed-end tubes contain a high-pressure encapsulated aqueous fluid (Fig. 1a), which displayed clearly segregated liquid and gas separated by well-defined curved interfaces. None of the open-end nanotubes (Fig. 1b) displayed any fluid inclusions.

EDS was used to identify the dark inclusions in the tube as an aqueous liquid (Fig. 1c). Although hydrogen cannot be measured using EDS, this technique can determine oxygen down to 0.1% concentrations. It can also distinguish between the oxygen traces trapped sparsely on the carbon walls (Fig. 1d) and the much higher oxygen quantities contained in the fluid (Fig. 1c). While oxygen may be adsorbed on the walls of both open and closed
tubes, the amount is insignificant compared to that trapped in the fluid phase. The EDS spectrum from the light area of the closed tube, such as in Fig. 1a, produced a very weak oxygen peak at the margin of detectability, while the spectrum taken from a portion of the nanotube containing dark fluid features a strong oxygen peak (Fig. 1c).

An important feature of hydrothermally produced nanotubes is their hydrophilic surface [15,18]. It is well known that formation of surface oxides renders the carbon surface hydrophilic [18]. The presence of hydrothermal fluid results in surface oxidation of the tubes, which is supported by detection of trace amounts of oxygen in the EDS spectra from open tubes (Fig. 1d). Hydrophilic adsorption centers (surface oxygen atoms or OH groups) are created as carboxylic or phenolic surface groups [18]. This results in a low contact angle between the carbon tube surface and the aqueous liquid (Fig. 1a).

Although EDS demonstrated presence of oxygen in the trapped fluid, quantitative chemical analysis of attoliters of fluids or gases in the nanotubes is not trivial. Therefore, we used thermodynamic simulation to determine the equilibrium composition of the tube contents. In the hydrothermal synthesis, all components of the fluid (H\textsubscript{2}O, H\textsubscript{2}, CO, CO\textsubscript{2}, CH\textsubscript{4} and minor quantities of higher hydrocarbons, formic acid, etc., see Fig. 2a) are in the supercritical state and show complete miscibility. As can be seen from Fig. 2a,b, carbon deposition leading to nanotube growth (if catalyst particles are present) is expected to occur upon cooling. If we consider the pressure–temperature dependence of the equilibrium:

\[
\text{CO}_2 + \text{CH}_4 \leftrightarrow 2\text{H}_2\text{O} + 2\text{C},
\]

the carbon precipitation can occur from a CH\textsubscript{4}/CO\textsubscript{2} mixture, which is predicted to be present inside the nanotubes, by lowering simultaneously pressure and temperature. As can be seen in Fig. 2b, water is the dominating component in the fluid in the whole temperature range, but especially at room temperature. This is in agreement with the EDS analysis of the tube contents and observation of water droplets in the synthesis capsule. However, CO\textsubscript{2} and CH\textsubscript{4} are expected to be present inside the tubes along with water (Fig. 2b). The composition of the fluid has showed a very week dependence on pressure at room temperature (Fig. 2c). However, the solubility of gases in water increases with increasing pressure and can affect the behavior of the liquid inside the tube. Estimates based on the C–H–O composition during the entrapment at the synthesis temperature and assuming an infinitely stiff circular cross-section of the tube predict internal pressures as high as 30 MPa [11]. The pressure will be lower if the fluid was trapped at lower temperatures. Since the critical temperature for CO\textsubscript{2} is 30.97 °C and the critical pressure is 7.374 MPa [19], carbon dioxide should be liquid inside the nanotube at the calculated internal pressure of about 30 MPa and mixed with water. The critical temperature for methane is −82.6 °C, thus it cannot be in the liquid state at room or higher temperatures in TEM and

![Fig. 1. Low magnification TEM micrographs showing a liquid plug in the nanotube (a) and a tip of the open tube (b). EDS spectrum in (c) comes from the dark fluid inclusion in the closed water-containing tube, while the one in (d) originates from the open nanotube.](image-url)
it is expected to be the major component of the gas phase. The solubility of methane in water is rather low (<0.4 mole% at the calculated pressure inside the tube and it will decrease with increase in temperature).

Lattice fringe imaging of the tube walls in the area of a liquid meniscus (Fig. 3) showed a strong interaction between the tube walls and the liquid. If a liquid inclusion was present in the area where some graphite planes terminated within the tube (inner diameter change, herring-bone structure or bending of the tube), swelling of the tube walls was always observed and the wetted graphite layers pointed away from the wall toward the tube axis (see arrows in Fig. 3a–c). It is believed that water/gases penetrated between the carbon layers causing this behavior. It is also important to note that this deformation of the inner carbon layers was observed independently of the amount of liquid present; a film less than 1 nm thick (Fig. 3a) caused the same lattice deformation as the inclusion filling the entire tube cross-section. This strong interaction between liquid and tube walls appears to be of chemical nature, and may explain the low mobility of the liquid/carbon interface near the wall observed in our previous study [13]. Understanding this behavior may be crucial for enabling fluid transport in nanopipes. It is important to note that the lattice fringe pattern changed from continuous thin lines typical of graphene (Fig. 3a) to dotted lines that suggest a non-planar structure (Fig. 3c). The formation of the first ‘dot’ at the termination of the carbon layer can be seen in Fig. 3b (marked with arrow). We suggest that this is the result of bonding of OH and oxygen to the dangling carbon bonds, forming hydroxyl and carbonyl groups. These groups make edges hydrophilic and allow hydrogen bonding to water molecules, which cluster at the carbon surface. The low-angle conical scroll structure of the tube walls leads to a sufficient number of plane terminations along the tube to make the whole tube hydrophilic. Thus, surfaces of hydrothermal nanotubes are hydrophilic, unlike clean or hydrogen-terminated surfaces of nanotubes produced by CVD, laser ablation of arc synthesis, which are hydrophobic. Attachment of large groups to the graphene edge and their hydrogen bonding to water molecules in

Fig. 2. Equilibrium reaction products as a function of temperature for the reaction between 1 mol ethylene glycol (EG) and 2 mol water. (a) Logarithmic plot of reaction products vs. temperature under 80 MPa pressure, (b) Temperature dependence of the molar content of main reaction products under 80 MPa pressure, (c) The pressure dependence of the reaction products at 300 K and 30 MPa, which shows that pressure has almost no effect on the predicted room temperature composition of the fluid trapped in the nanotubes.
the thin liquid layer covering the tube wall (or to water molecules in the liquid inclusion) pulls the inner cylinder toward the center of the tube, away from the tube surface, as schematically shown in Fig. 3. This allows water and carbon dioxide to penetrate between the carbon layers and leads to further swelling of the structure (Fig. 3c).

In some locations, we observed uniform swelling and intercalation of tube walls resulting in almost doubling of the lattice spacing (Fig. 3d). A similar intercalation of multiwall nanotubes resulting in the increase of the lattice spacing up to 0.95 nm was achieved using FeCl₃ [20]. Thus, water and gases can penetrate between carbon layers forming a structure that may be similar to graphite oxide (GO) [21,22]. The observed interplanar spacing of 0.61 nm (Fig. 3d) is in agreement with the 0.6–0.7 nm spacing in GO. Another explanation for the increased spacing may be due to penetration of a monolayer of water molecules.
between graphene sheets. Considering that the size of oxygen governs that of a water molecule (about 0.3 nm), the spacing increase due to water penetration should be \(0.335 + 0.3 \text{ nm} = 0.635 \text{ nm}\). This value is comparable with the one measured from Fig. 3b. The fact that no bending of graphene sheets was found in dry open nanotubes (Fig. 3c) confirms the hypothesis of intercalation with O–H species. The formation of a graphite intercalation compound may be the reason for a weak Raman band at 1620 cm\(^{-1}\) observed in the Raman spectra of hydrothermal carbon nanotubes produced from ethylene glycol solutions. To the best of our knowledge, intercalation of graphite or carbon nanotubes by hydrothermal treatment has never been reported. Intercalation with O–H species can lead to change in electronic and chemical properties of the tubes. Graphite oxide is known to be non-conductive [22], thus an insulating layer can be formed inside the tube.

Multiwall nanotubes are known to have a low chemical reactivity typical of graphite [17]. However, heating with the electron beam in the TEM can raise the temperature inside the tube above 600–700 °C. Thermodynamic analysis (Fig. 2a) predicts that the temperature increase will result in a chemical reaction between the tube and the supercritical fluid and dissolution of carbon. This reaction leads to dissolution of the carbon wall in the area of the inclusion (Fig. 4) and, ultimately, puncture of the tube wall and loss of the tube fluid to the microscope environment. EDS shows an immediate decrease of the oxygen peak to almost background levels after tube puncture. We speculate that in a freestanding and deformed carbon cylinder (Fig. 3c), hydrogenation or oxidation of carbene rings is possible, resulting in transition from an sp\(^2\)-hybridized flat graphite network to sp\(^3\)-hybridized hydrated layer, which is the first step toward dissolution of the wall. This initial process would be similar to hydrogenation of aromatic rings under pressure in the presence of a catalyst, which produces cyclohexanes [23]. Controlled dissolution of wall sections of multiwall nanotubes by reaction with the supercritical fluid can be used to produce chambers inside the tubes (Fig. 4b), dissolve internal closures in the tubes, or open the closed tubes.

### 4. Conclusions

Closed hydrothermal nanotubes with encapsulated aqueous fluid allow unique in situ chemical experiments in TEM. The fluid contains water and carbon dioxide, which form liquid inclusions, as well as methane, which is the main component of the gas phase. Oxidized surfaces of hydrothermal nanotubes are hydrophilic and have a great potential for nanofluidic applications. Interaction between the graphitic tube walls and aqueous liquid, which penetrates between the layers, results in swelling of the inner wall layers, the bending of graphite cylinders toward the center of the tube, and intercalation of several inner layers of the tubes with the interplanar spacing increasing to 0.61 nm. By fast heating, a chemical interaction between the tube’s wall and the water-based...
supercritical fluid can be initiated. This chemical interaction leads to dissolution of the tube wall, increase in the internal diameter of the tube in the vicinity of the liquid inclusion, and the reduction of the number of layers in the tube wall. It can be used for micromachining inner surfaces of the closed tubes.

Acknowledgements

We thank Prof. C.M. Megaridis, University of Illinois at Chicago, for helpful discussions. This work was supported by the US National Science Foundation under grant CTS-0196006. The microscopes used are operated by the Research Resources Center of the University of Illinois at Chicago.

References