Wetting of CVD Carbon Films by Polar and Nonpolar Liquids and Implications for Carbon Nanopipes

D. Mattia,† H. H. Bau,‡ and Y. Gogotsi*†

Materials Science and Engineering Department and A.J. Drexel Nanotechnology Institute, Drexel University, 3141 Chestnut Street, Philadelphia, Pennsylvania 19104, and Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, 220 South 33rd Street, Philadelphia, Pennsylvania 19104

Received July 6, 2005. In Final Form: November 9, 2005

The handling, dispersion, manipulation, and functionalization of carbon nanotubes and nanopipes often require the use of solvents. Therefore, a good understanding of the wetting properties of the carbon nanotubes is needed. Such knowledge is also essential for the design of nanotube-based nanofluidic devices, which hold the promise of revolutionizing chemical analysis, separation, drug delivery, filtration, and sensing. In this work, we investigated the wetting behavior of individual nanotubes produced by the chemical vapor deposition (CVD) on porous alumina templates and of thin carbon films produced by the same technique. The carbon pipes and films have the same chemistry and structure as determined by Raman and infrared spectroscopies and, when similarly treated, demonstrate the same qualitative wetting behavior, as determined by optical microscopy. Thus, measurements conducted on the carbon film surface are relevant to the nanopipes. In the case of the nanopipes, filling with various liquids was monitored. Contact angle experiments with both polar (water, glycerol, ethylene glycol, ethanol, tetra-hydro furan, and 2-propanol alcohol) and nonpolar liquids (cyclohexane, hexadecane, poly(dimethylsiloxane), and a fluoro-silicone) were conducted on films using the sessile drop method. The contact angles on the CVD carbon films ranged from 0 to 79°. The exposure of the carbon films to a NaOH solution, typically used to dissolve the alumina template, led to a significant decrease of the contact angle, especially in the case of polar liquids.

Introduction

The wetting properties of carbon nanotubes (CNTs) and carbon nanopipes (CNPs) are important in applications ranging from composite materials, in which uniform dispersion in a monomer or solvent must be achieved, to nanodevices,1−3 which require both fluid-based handling and the ability to fill the tubes with liquids. CNPs with diameters ranging from tens to hundreds of nanometers may be used in nanodevices as interconnects or probes that transport fluids in/out of the devices.4 In contrast to multimwalled CNTs, template-grown tubes have the advantage of being straight, relatively long (∼60 μm), and open at their ends, hence the term carbon nanopipe. Although lithography techniques can be pushed to the nanoscale, CNTs and CNPs may represent an easier and, potentially, more cost-effective solution for many applications such as lab-on-a-chip, chemical and biological detection, and drug delivery systems.

Although the surface tension for water is well below the value of 200 mN/m identified by Dujardin et al.5 as the threshold for the entry of liquids into SWNTs, in analogy with basal planes of graphite, CNTs and CNPs are generally believed not to be wetted by polar fluids and water. However, transmission electron microscopy (TEM) images of water inside CNPs exhibited good wetting and low contact angles.6 Previous studies have shown that it is possible to condense water and ethylene glycol on and inside different kinds of CNTs and CNPs7 and to fill CNP with glycerol and water by capillary forces.8 Recently, Barber et al.9 inferred wetting of the internal walls of 20−60 nm CNTs from the unusual response of nanotubes attached to an atomic force microscope (AFM) tip immersed in water. Unfortunately, the direct measurement of the contact angle inside the narrow quasi-cylindrical bore of nanotubes and CNPs remains difficult and can be affected by experimental conditions such as e-beam irradiation in environmental scanning electron microscopy (ESEM)6 and TEM10,11 studies. A review of the literature for contact angle values of water on graphite reveals a wide scatter, ranging from 35° to 40° to 65°,14 and up to 80−85°.15−17 These variations are apparently due to factors such as differences in experimental setups, surface preparation, and the type and quality of the graphite. One school of thought attributes the contact angles of ∼84° and 30° to the basal plane and the edge sites of the graphite structures, respectively.13 A second school of thought

assumes that the true value of the contact angle of water on graphite is around $30^\circ$ to $35^\circ$ and that the higher value of $80^\circ$ to $84^\circ$ is due to chemisorption of hydrogen or adsorbed hydrocarbons on the surface of the graphite, which enhances the hydrophobic behavior of the substrate.\textsuperscript{18}

Molecular dynamics simulations also appear to be nonconclusive; although Werder et al.\textsuperscript{19} found that water should not wet SWNTs, in a subsequent paper,\textsuperscript{20} the same authors suggested that wetting predictions may vary substantially as a function of the choice of the potentials and initial parameters used in molecular dynamics calculations. Other simulations suggest that hydrogen surface termination increases wetting compared to a pristine basal plane of graphite.\textsuperscript{21} Walther et al.\textsuperscript{22} suggested that water interactions with CNTs and graphite sheets are similar and the results obtained with the latter system should be applicable to the former. Noon et al.\textsuperscript{23} found that water exists inside SWNTs at 300 K and 1 atm and forms highly hydrogen-bonded, ice-like networks. Supple et al.\textsuperscript{24} reported that SWNTs easily imbibe oil.

For both CNTs and CNPs, contact angles well below $90^\circ$ have been consistently reported. In particular, the observations of low contact angles of water inside CNPs\textsuperscript{7} have raised the question of what mechanism leads to such low contact angles. To respond to this question, to address the seemingly contradictory results reported in the literature, and to provide important data to designers of nanofluidic systems, we carried out a systematic study of the wetting characteristics of both polar and nonpolar liquids on CVD carbon films deposited on different substrates under the same conditions used for the synthesis of CNPs in alumina templates. The anticipated behavior of the various liquids inside carbon nanopipes was confirmed by carrying out filling experiments on CVD CNPs.

**Experimental Section**

Carbon films and CNPs deposited by the CVD process under the same conditions have been used to perform contact angle and liquid condensation measurements. The behavior of several liquids on CVD carbon surfaces has been studied.

**Materials.** CNPs and films were produced by noncatalytic CVD using commercial alumina membranes (Whatman Anodisc, nominal pore diameter: 200 nm $\pm$ 10%; 60 $\mu$m length) as templates for nanofiber synthesis.\textsuperscript{25,26} (Figure 1a). Polished (4000 SiC paper) and degreased glassy carbon (GC) tokens (GL-200 from Toyano Tanso Co., Japan), polished Si wafers and quartz (Chemglass, NJ) were used as substrates for carbon film deposition. To separate the CNPs from the template, alumina was dissolved in boiling 1 M NaOH solution. The resulting CNPs were perfectly straight with a maximum length of 60 $\mu$m, an external diameter of about 220 $\mu$m (Figure 1b). A typical wall thickness of 15–20 nm.

Contact angles were studied for the following liquids: deionized water, ethanol, 1,2-ethanediol (IPA), tetra-hydro furan (THF), glycerol, ethylene glycol, and cyclohexane (spectroscopic grade from Fisher Scientific); hexadecane (spectroscopic gold label grade from Sigma); poly(diethylsiloxane), PDMS-T01, and poly (3,3,3-trifluoropropylsiloxane), FPMS-123 (from Gelest Inc, PA). All liquids were used without further purification.

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\textsuperscript{24} Supple, S.; Quirke, N. Phys. Rev. Lett. 2003, 90 (21), 214501.
Figure 2. Raman spectra of the carbon materials under study: (1) glassy carbon (GC) substrate; (2) as-deposited CVD carbon film on GC; (3) CNPs deposited in the membrane by CVD before NaOH treatment; (4) as-deposited CVD carbon film on a quartz slide; (5) CVD CNP after membrane dissolution in NaOH.

Figure 3. FTIR spectra of carbon films: (1) GC; (2) as-deposited CVD film on GC; (3) CVD film on GC after NaOH treatment.

The broad band at 2950 cm$^{-1}$ could be attributed to a D + G combination mode$^{28}$ or more likely to C$\equiv$H stretching,$^{29}$ consistent with FTIR results (Figure 3). Raman spectra for the film deposited by CVD on GC (Figure 2, curve 2) and on quartz (Figure 2, curve 4) are similar to the spectrum collected from individual CNP after NaOH treatment (Figure 2, curve 5). Therefore, we concluded that carbon films deposited by CVD on glassy carbon, quartz, and silicon have the same chemistry and structure as the CNP obtained from the template and can provide information concerning the wetting properties of CNPs.

The peak around 1600–1620 cm$^{-1}$ in FTIR spectra (Figure 3) of the glassy carbon substrate (1), the as-deposited film on GC (2), and the film after NaOH treatment (3) is attributed to the C$\equiv$C stretching in the hexagonal graphite and is in agreement with the G-band in the Raman spectra$^{30}$ (Figure 2). The peak around 3000–3100 cm$^{-1}$, which can be deconvoluted into two peaks at 2950 and 3090 cm$^{-1}$, is assigned to C$\equiv$H stretch in aromatic structures,$^{31}$ which generally produces narrower peaks.$^{30}$ We surmise that the broadness of this peak is due to the disordered structure of the CVD film as is often observed in a-C$\equiv$H films.$^{27}$ This is also confirmed by the increase of the C$\equiv$H:C=C peak ratio after CVD deposition on the glassy carbon substrate, which is in agreement with the well-known formation of C$\equiv$H bonds as a result of CVD synthesis from hydrocarbon precursors.$^{27}$ The two shoulders at about 3350 cm$^{-1}$ can be attributed to O–H stretching, although quantitative conclusions cannot be drawn due to the background noise from the water in the atmosphere.

Results and Discussion

Material Characterization. Image analysis of the template after vapor CVD deposition (Figure 1a) indicated that the fractional surface coverage of the alumina membrane walls ($d_{mem}$) was on the order of 35–40%, the rest being hollow cavities ($d_{h}$). The distribution of the CNPs’ external diameters as measured on the membrane surface after CVD resulted in a mean value of 203 nm and a standard deviation 10 nm (Figure 1c). Similar analysis of free-standing CNPs (Figure 1b) yielded slightly larger external diameters, 220 ± 20 nm. The CNPs and thin films produced by CVD (Figure 1d) were made of pyrolitic carbon$^{27}$ that has a turbostratic and disordered structure. Raman spectra of the thin carbon film deposited by CVD on a glassy carbon substrate (2) or on a quartz slide (4), of CNPs deposited in the membrane by CVD before NaOH treatment (3), and of individual CNPs after NaOH treatment (5) were almost identical (Figure 2) and distinctly different from that of the glassy carbon (GC) (1). The band at 1582 cm$^{-1}$ for GC and at 1600 cm$^{-1}$ for the coating and CNPs resulted from in-plane vibrations of graphite (G band). The peak around 1350 cm$^{-1}$ is attributed to the disorder-induced band of carbon materials (D band). Broad D and G bands suggest a disordered structure of CVD carbon in agreement with TEM micrographs.$^{7}$ Second-order bands at 2700 and 3230–3250 cm$^{-1}$ were attributed to 2D and 2D$'$ modes, respectively.$^{28}$

Wetting Setup. The contact angle measurements were carried out using the sessile drop method in air at room temperature with 5 µL droplets. Prior to the measurements, the samples were dried overnight at 70 °C, and then were immediately placed on a goniometer. Still images and movies were acquired using a 1/2 in. CCD camera. The contact angle was inferred from the photographs.

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Contact Angle Experiments. Table 1 documents the contact angle values for water, glycerol, and FPMS on polished glassy carbon and as-deposited CVD film on GC, quartz, polished silicon wafer, and the alumina membrane template. The images in Figure 4 illustrate the method used for the contact angle measurement. Although it is well-known that surface roughness of the substrates affects the contact angle,$^{25}$ the measured contact angle values were similar for all investigated surfaces except the alumina membrane. In particular, the contact angle measured for water is consistent with the value of 80.1 ± 3.6° estimated for MWNT attached to an AFM tip and immersed in water as reported by Barber et al.$^{33}$

References

NaOH, as will be shown in the following section. It readily fills (along with other liquids) nanopipes treated with pores of the membrane because of the high contact angle, whereas carbon, quartz, and silicon (Table 1). Similar calculations for measured for water on carbon films deposited on smooth glassy membrane (prior to the NaOH treatment), a much higher value of the contact angle was measured. This high value is attributable to its porous and rough surface (Figure 1a). Most likely, air was trapped in the pores beneath the drop, causing the drop to be partially cushioned by air and resulting in super-hydrophobic behavior. Los, A.; Quere, D. Nat. Mater. 2003, 2, 546–551.

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Table 1. Contact Angle of Water, Glycerol, and FPMS on Various Surfaces

<table>
<thead>
<tr>
<th>Surface</th>
<th>Water</th>
<th>Glycerol</th>
<th>FPMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy carbon</td>
<td>76</td>
<td>59</td>
<td>9.0</td>
</tr>
<tr>
<td>CVD film on glassy carbon</td>
<td>79</td>
<td>64</td>
<td>9.2</td>
</tr>
<tr>
<td>CVD film on quartz</td>
<td>76</td>
<td>67</td>
<td>8.9</td>
</tr>
<tr>
<td>CVD film on Si wafer</td>
<td>75</td>
<td>67</td>
<td>9.1</td>
</tr>
<tr>
<td>CVD film on the membrane</td>
<td>122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CVD film on the membrane corrected</td>
<td>~72</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Contact angle values for water and glycerin have a standard deviation ±2°. Data for FPMS has a standard deviation of ±0.5°. Los, A.; Quere, D. Nat. Mater. 2003, 2, 546–551.

The value of 72° for water is consistent with the values for FPMS and PDMS. Los, A.; Quere, D. Nat. Mater. 2003, 2, 546–551.

Figure 4. Optical images of water droplets on (a) as-deposited CVD film on glassy carbon and (b) CVD film on glassy carbon after NaOH treatment.

In the case of a rough surface, the Cassie equation

\[ \gamma_{LV} \cos \theta_c = \phi_m (\gamma_{SV} - \gamma_{SL})_{\text{membrane}} + \phi_a (\gamma_{SV} - \gamma_{SL})_{\text{air}} \cos \theta_c = \phi_m \cos \theta_m + \phi_a \cos \theta_a \tag{1} \]
can be used to evaluate the actual contact angle between the drop and the carbon film. In the above, \( \gamma \) is the surface tension, and subscripts S, L, and V denote the solid, liquid, and vapor, respectively. Thus, \( \gamma_{SL} \) stands for the surface tension at the solid–liquid interface and \( \gamma_{SV} \) for the surface tension at the solid–vapor interface. \( \theta_c \) is the measured contact angle for the liquid drop on the porous surface (\( \theta_c \sim 122^\circ \) for water), and \( \phi_m \) and \( \phi_a \) are the fractional surface coverage of the membrane and air, respectively. Water forms a contact angle of 180° with air (recall rain drops), hence \( \theta_c = 180^\circ \). Los, A.; Quere, D. Nat. Mater. 2003, 2, 546–551.

The solution of eq 1 yields \( \theta_m \sim 72^\circ \). Water is not dragged inside the nanotubes covering the pores of the membrane because of the high contact angle, whereas it readily fills (along with other liquids) nanopipes treated with NaOH, as will be shown in the following section.

The value of 72° for water is consistent with the values measured for water on carbon films deposited on smooth glassy carbon, quartz, and silicon (Table 1). Similar calculations for glycerol and FPMS could not be performed due to the intrinsic limitation of the Cassie–Baxter model.

Surface Modification. Contact angle data for all of the investigated liquids on CVD carbon before and after NaOH treatment are summarized in Table 2. Although contact angle measurements of liquids with a relatively low vapor pressure, such as water, glycerol, and ethylene glycol, can be done in a very accurate way, as can be seen from shapes of water droplets in Figure 4, measurements of the contact angle of highly volatile liquids, such as ethanol, have a lower degree of accuracy.

Plotting these data as the cosine of the contact angle vs the surface tension (Zisman plot) shows a linear relationship between \( \cos(\theta) \) and the surface tension for lower vapor pressure polar liquids (Figure 5a) and all nonpolar liquids (Figure 5b), in agreement with Zisman et al. Los, A.; Quere, D. Nat. Mater. 2003, 2, 457–460.

The data can be correlated in the form

\[ \cos \theta = 1 - \beta (\gamma_c - \gamma) \tag{2} \]

where \( \gamma_c \) is the critical surface tension and \( \beta \) is a correlation constant.

Table 2. Contact Angle of Various Liquids on CVD Carbon Films

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Polarity</th>
<th>Surface Tension [mN/m]</th>
<th>Contact Angle [°]</th>
<th>as-deposited</th>
<th>after NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Polar</td>
<td>72</td>
<td>79</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>21.97</td>
<td>12</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>EG</td>
<td></td>
<td>47.99</td>
<td>41</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>IPA</td>
<td></td>
<td>23.28</td>
<td>8</td>
<td>~0</td>
<td></td>
</tr>
<tr>
<td>Glycerol</td>
<td></td>
<td>62.5</td>
<td>64</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td></td>
<td>26.4</td>
<td>12</td>
<td>~0</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td></td>
<td>24.65</td>
<td>10</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>PDMS-T01</td>
<td>Nonpolar</td>
<td>17.4</td>
<td>9</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Hexadecane</td>
<td></td>
<td>27.05</td>
<td>12</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>FPMS-123</td>
<td></td>
<td>25.7</td>
<td>9</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>


Literature data shows that glassy carbon produced at °
no substantial difference, both values being slightly below 80
on the as-deposited CVD film prior to NaOH treatment showed
slight increase in the contact angle. In the case of the nonpolar fluids, the NaOH treatment resulted in a
poor wetting of the CVD film with water is attributed to the
hydrophobic layer found by FTIR (Figure 3). It is consistent with molecular dynamics studies that predict contact angles ranging from 83° to 102° for water on the basal plane of graphite when 10% of the top layer carbon atoms are covered with hydrogen. 

Contact angle measurements for water on glassy carbon and on the as-deposited CVD film prior to NaOH treatment showed no substantial difference, both values being slightly below 80° (Table 1). Literature data shows that glassy carbon produced at 2000 °C is poorly wetted and minimally absorbs water. The poor wetting of the CVD film with water is attributed to the C–H hydrophobic layer found by FTIR (Figure 3). It is consistent with molecular dynamics studies that predict contact angles ranging from 83° to 102° for water on the basal plane of graphite when 10% of the top layer carbon atoms are covered with hydrogen. 

Filling of Nanopipes. Due to the relatively large diameter and thin walls (15–20 nm) of the CVD CNPs (Figure 1b), it was possible to monitor the filling process with an optical microscope. The CNPs filled readily with all the liquids for which contact angle measurements have been performed, including nonpolar liquids.

Once the nanopipe had been placed on the substrate, a micropipet filled with the liquid (e.g., ethylene glycol) was placed in contact with one of the nanopipe’s end. The liquid filled readily the nanopipe by capillarity (Figure 6a). Once the pipet was removed fast evaporation of ethylene glycol was observed (Figure 6, panels b and c). In a similar experiment with a nonpolar liquid, cyclohexane first spread on the gold substrate and then filled the nanopipe denoted (i) in Figure 7a. The liquid then condensed in the nanopipe (iii) on the left of the image from one side (Figure 7b) until the tube completely filled (Figure 7, panels c and d).

The capillary filling of the CNPs is consistent with the low contact angles measured on the CVD carbon films (Table 2).

Unfortunately, optical microscopy did not provide sufficient resolution to measure the diameter of the CNPs and the contact angles of liquids inside them. Although it is impossible to resolve details of the CNP with the ~200 nm diameter, it is nonetheless possible to see a difference in the contrast between the filled and empty tubes.

Evaporation of polar fluids such as water or ethylene glycol occurred very rapidly in comparison to hydrocarbons. Although cyclohexane is ~1000 times more volatile than ethylene glycol, the former remained in the interior of the CNPs for a period of few hours, under atmospheric pressure. Ethylene glycol, on the other hand, evaporated rapidly after filling of the tube (Figure 6). This suggests a strong interaction between hydrocarbons and the CVD tubes’ surface, which requires further study. The fact that liquids readily and preferentially fill CVD CNPs allows their use as probes for sensing vapor in the environment, including humidity measurements. Easy filling with various liquids enables the use of CNPs as nanopipets for delivering attoliter volumes of drugs to single cells or probing cells by imbibing extremely small amounts of biofluids. The CNPs can also be used as chemical reactors for controlled synthesis and as biosensors. Finally, the CNPs can be filled with various suspensions to form new materials with tailored properties such as magnetic and fluorescent tubes.

Conclusions

Contact angle experiments on thin CVD carbon films, which are chemically analogous to CVD CNPs, provide important information on the wettability of CVD film walls. All of the investigated liquids, including water, wet disordered CVD carbons with the contact angle ranging from 0° to ~80°. NaOH-induced surface modification of the CVD carbons led to a significant decrease in the contact angle for polar liquids but did not considerably affect their wetting by nonpolar liquids, such as hydrocarbons. It has also been demonstrated that the internal cavities of CNPs can be readily filled with both polar and nonpolar liquids. Thus, CNPs can readily imbibe a variety of fluids and preferential condensation of vapor occurs inside CNP channels.

Acknowledgment. This research was supported by NSF NIRT Grant CTS-0210579. The authors thank Dr. B. M. Kim, University of Pennsylvania, for the nanopipe filling experiments and Ms. M.P. Rossi, Drexel University, for helpful discussions. Microscopes and spectrometers belong to the Materials Characterization Facility of the A. J. Drexel Nanotechnology Institute.