Electromagnetic modulation of carbon nanotube wetting

Yi-Fan Li, a Chia-I Hung, a Hsin-Fu Kuo, a Sen-Hong Syue, a Wen-Kuang Hsu, a* Shin-Liang Kuo b and Shu-Chuan Huang b

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NH3 H2O treated carbon nanotubes form an electric double layer in the presence of an electric field and tube wetting is therefore improved. Proton concentration on tube surfaces can be further modulated by a Lorentz force and is verified by multi-transition of an hydrophobic into an hydrophilic phase.

1. Introduction

A recent study on carbon nanotubes (CNTs) known as graphene sheets rolled into a seamless cylinder has largely focused on solution properties and it is now understood that wetting of conjugated surfaces is dominated by a dispersive force and tube curvature induces an extra contribution of polar energy to the critical surface tension.1 CNTs can be hydrophilized via oxygenation whereas surface wetting is improved at the expense of severe lattice damage.2 In this work, an electromagnetic modification of CNTs is demonstrated and the procedure involves a generation of an electric double layer (EDL) on CNT surfaces via NH3 H2O treatment. We find that protons accumulate at nanotube surfaces in the presence of an electric field and the liquid–droplet interface is therefore dominated by polar character. The proton concentration on tube surfaces can be finely tuned by a Lorentz force and is supported by the multi-transition of an hydrophobic into an hydrophilic phase.

2. Experimental

Single-walled CNTs (SWCNTs, 1.1–1.4 nm in diameter and 1–4 μm in length, 90% purity) made by electric arc discharge of Ni–Yi embedded graphite rods are heated in an ambient environment (300 °C, 40 min) to remove carbonaceous impurities and oxidized SWCNTs are subsequently dispersed in deionized water (DW) containing 1 wt% of sodium dodecyl sulfate (SDS).4 SWCNT dispersion (1 mg mL−1) is transferred onto a polyethylene terephthalate (PET) film via roller printing and SDS is removed by rinsing the SWCNT coated film with DW. Electrical connections are made by depositing silver paste onto nanotube film edges via a masking technique and the film temperature is measured by a digital thermocouple (Agilent-34970A) attached underneath. Comparative experiments were carried out on ammonia treated SWCNT films and the procedure is as follows. SWCNTs are deposited onto PET film by a similar method to that described above and NH3 H2O (Showa, 28%) is sprayed onto the composite film.5 The treated film is placed in a fume cupboard for 1 h to remove excess ammonia and subsequently subjected to wetting tests. An optical microscope equipped with a charged coupled device (CCD) camera is employed to measure film wettability and DW is selected as the testing droplet. Ethylene glycol (EG) known to possess a greater dispersive character is also studied for comparison.5

3. Results and discussion

Fig. 1a shows the experimental set up and the contact angle (CA) measurement is carried out within an area of 1 × 1 cm2. The SWCNT-coated PET film shows an excellent flexibility (Fig. 1b) and transmittance at the visible-light regime has been estimated to be 65% (Fig. 1c). Fig. 1d displays the coating of SWCNTs and the sheet resistance revealed by the four-probe technique is 4500 ± 500 Ω sq−1 before and 680 ± 20 Ω sq−1 after SDS removal. Fig. 2a and 2f show DW and EG droplets on untreated SWCNT film and the CA is found to be 93.1° and 69.7° (Table 1); the CA(DW) > CA(EG) being a consequence of the stronger dispersive interaction of the conjugated CNT surfaces with the ethylene moiety of EG (Table 2).5 The CA on ammonia treated film decreases to 83.1° for DW and 56.3° for EG, corresponding to 10.7% and 19.2% reductions (Fig. 2b and 2g). We have calculated

Fig. 1 Experimental set-up (a), SWCNT coated PET film (b), UV-VIS spectra of SWCNT-coated PET film (c), SEM image of the coating of SWCNTs (d).
Table 1 CA and calculated surface tensions of SWCNT film and DW and EG

<table>
<thead>
<tr>
<th>Samples</th>
<th>CA&lt;sub&gt;DW&lt;/sub&gt; (°)</th>
<th>CA&lt;sub&gt;EG&lt;/sub&gt; (°)</th>
<th>γ&lt;sub&gt;sv&lt;/sub&gt; (mN m&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>γ&lt;sub&gt;lp&lt;/sub&gt; (mN m&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>γ&lt;sub&gt;lv&lt;/sub&gt; (mN m&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>93.1</td>
<td>69.7</td>
<td>17.77</td>
<td>4.29</td>
<td>22.07</td>
</tr>
<tr>
<td>Treated</td>
<td>83.1</td>
<td>56.3</td>
<td>22.12</td>
<td>6.98</td>
<td>29.11</td>
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<tr>
<td>10 V</td>
<td>41.6</td>
<td>33.2</td>
<td>9.62</td>
<td>47.49</td>
<td>57.11</td>
</tr>
<tr>
<td>12 V</td>
<td>38.3</td>
<td>30.3</td>
<td>9.48</td>
<td>50.33</td>
<td>59.81</td>
</tr>
<tr>
<td>14 V</td>
<td>35.0</td>
<td>25.8</td>
<td>9.89</td>
<td>52.22</td>
<td>62.11</td>
</tr>
</tbody>
</table>

Table 2 The γ<sub>sv</sub>, γ<sub>lp</sub>, and γ<sub>lv</sub> of DW and EG

<table>
<thead>
<tr>
<th>Liquid</th>
<th>γ&lt;sub&gt;sv&lt;/sub&gt; (mN m&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>γ&lt;sub&gt;lp&lt;/sub&gt; (mN m&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>γ&lt;sub&gt;lv&lt;/sub&gt; (mN m&lt;sup&gt;-1&lt;/sup&gt;)</th>
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</thead>
<tbody>
<tr>
<td>DW</td>
<td>21.8</td>
<td>51</td>
<td>72.8</td>
</tr>
<tr>
<td>EG</td>
<td>33.8</td>
<td>14.2</td>
<td>48</td>
</tr>
</tbody>
</table>

24.47% (Table 1). According to previous FTIR data, immersion of SWCNTs into ammonia water results in NH₃ adsorption and adsorbed molecules are found to interact with the tube via a long pair on the N-atoms. This is supported by a large blue-shift of the umbrella mode and broadening of the N–H bending modes and the adsorption energy has been estimated to be comparable with hydrogen bonding character, accounting for the enhancement detected here. It is noteworthy that adsorbed NH₃ essentially behaves as an electron donor and tends to capture a proton from the attached droplet in the presence of an electric field. This yields an EDL and Coulomb attraction (F<sub>att</sub>) established between NH₄⁺ and a negatively charged SWCNT film is therefore expected to facilitate the droplet wetting and permeation. Fig. 2c and 2h show DW and EG droplets on treated films with an applied voltage of 10 V, corresponding to 5 × 10<sup>5</sup> V µm<sup>-1</sup>. We find that the DW droplet is dragged by the electric field and the asymmetric structure becomes apparent when the field intensity increases (Fig. 2c–e). In contrast, the EG droplet remains beaded, indicative of a lower γ<sub>lv</sub> at the tube–liquid interface. Compared with the untreated film, the CA on NH₃–H₂O-treated film is reduced by 55% for DW and 51% for EG at 10 V whereas the γ<sub>sv</sub> is promoted by a factor of ten (Table 1). CA reduction by Joule heating is unlikely because droplet vaporization is absent and the film temperature as revealed by a thermocouple fluctuates only by ±2 °C. CA further decreases as the applied voltage increases and reaches 35° and 25.8° at 14 V for DW and EG. In total, the γ<sub>sv</sub> is promoted by a factor of 11 and the γ<sub>sv</sub>/γ<sub>lv</sub> ratio decreases to 0.18–0.2 at 10–14 V. Additional evidence in support of EDL formation on tubes comes from the fact that an electric field applied to ammonia untreated SWCNT film causes only a 2–3% CA reduction and γ<sub>sv</sub> remains unchanged.

CA change however is irreversible and protons do not detach from tube surfaces upon field reversing, possibly due to (i) liquid permeation into the SWCNT film and (ii) γ ≫ F<sub>att</sub>. According to the Right-Hand rule application of the magnetic field perpendicular to the electric field produces a Lorentz force and charged particles are accelerated in the same orientation as the electric field. In the next experiments, we find that the electric field induced proton accumulation at the SWCNT surfaces can be deferred or accelerated by an external magnetic field, depending on the applied direction. For example, a reverse...
application of the magnetic field produces an upward Lorentz force and protons therefore remain dispersed in the droplet (Fig. 3a). Proton precipitation is accelerated at forward magnetic field and \( \gamma_p \) enhancement, hence CA reduction, becomes significant (Fig. 3b). Fig. 3c shows the magnetic field modulated CA and the electric field intensity is set at \( 5 \times 10^5 \) V \( \mu \)m\(^{-1} \). At zero magnetic-field the CA is 42° for DW and 33.4° for EG, consistent with the value detected at 10 V (Table 1). Upon applying the magnetic field the CA decreases significantly with increasing field intensity at forward application and we obtain 38.7° and 30.4° at 90 Oe, 36.3° and 28.5° at 140 Oe, and 30.8° and 23.4° at 200 Oe for DW and EG. In contrast, the CA decrease is insignificant at reverse application and measurements give 47° and 37.2° at –90 Oe, 56.7° and 41.5° at –140 Oe, and 70.5° and 47.4° at –200 Oe for DW and EG respectively, i.e. the CA decrement shrinks as

**Fig. 3** A reverse magnetic field application to an electrically connected electric double layer (EDL)-SWCNT device (a), a forward magnetic field application to an electrically connected EDL-SWCNT device (b), CA variation of deionized water (DW) and ethylene glycol (EG) versus magnetic field intensity in the presence of a constant electric field \( (5 \times 10^5 \) V \( \mu \)m\(^{-1} \) \) (c).

**Fig. 4** Electromagnetic field controlled CAs from the hydrophobic to the hydrophilic phase and corresponding images: DW (top panel) and EG (lower panel).

**Fig. 5** Volumetric flow rate \( (V_f) \) vs. magnetic field intensity (a), variation of \( \gamma_p \), \( \gamma_d \), and \( \gamma_v \) with magnetic field (b), and variation of the calculated surface energy with the applied magnetic force (c).
the field intensity increases. Results are reproducible when the magnetic field is repeatedly tuned from 200 Oe to −200 Oe, and vice versa. The Lorentz force induced concentration gradient of the proton at the interface is also supported by the fact that the $\gamma_{sv}$ remains around 3.17 when the electric field is switched off and the device experiences a magnetic force only. Fig. 4 plots CA vs. magnetic field modulated surface energy and the gap between $\gamma_{sv}$ decreases by 66.8% at −200 Oe. As described above the $\gamma_{sv}$ originates from the van der Waals interaction and cannot be altered by field application. Accordingly, a small decrease in $\gamma_{sv}$ at the forward field is attributable to the screening effect by accumulated protons (Fig. 5c). When protons detach, the hydrophobic CNT surfaces are exposed and $\gamma_{sv}$ increases accordingly, consistent with Fig. 5b.

Acknowledgements

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References