Insights into Graphene Wettability Transparency by Locally Probing its Surface Free Energy

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Supporting Information

Contents

S.I Raman of exfoliated bilayer graphene coated SiO₂

S.II Peakforce tapping mode of CVD-grown graphene coated SiO₂

S.III Two possible ice-like water structures on suspended graphene surface

S.IV Time-resolved Fourier-transform infrared spectroscopy of fresh graphite flake surface

S.V Transferred graphene on SiO₂/Si with and without annealing

S.VI List of all used pseudo-potentials in QuantumEspresso package
S.I. Raman of exfoliated bilayer graphene coated SiO$_2$

For bilayer exfoliated graphene coated SiO$_2$, the related Raman spectra and Raman mapping image is shown in Fig. S1. The force of adhesion distributions in Fig. 1(d) of the manuscript are extracted from the regions of exfoliated graphene on SiO$_2$ with monolayer, bilayer, and multilayer graphene, respectively.

Fig. S1 (a) I(G)/I(2D) Raman mapping image of exfoliated graphene on SiO$_2$. (b) Raman spectra of bilayer graphene on SiO$_2$. 
S.II. Peakforce tapping mode of CVD-grown graphene coated SiO$_2$

Fig. S2 Force of adhesion distribution of CVD-grown graphene on SiO$_2$ under peakforce tapping mode.

The force of adhesion characterization of CVD-grown graphene on SiO$_2$ is conducted using PeakForce Tapping mode with Bruker’s atomic force microscopy. The tip-sample distance is modulated in a sinusoidal motion at amplitudes normally below 100nm and at frequencies of 1 or 2kHz in PeakForce Tapping mode. These features ensure accurate and direct control of the tip-sample interaction force, enabling imaging in fluids at forces of 100pN or less.
S.III. Two possible ice-like water structures on suspended graphene surface

Fig. S3 (a) methodology of contact angle prediction with DFT simulation. (b) Adsorption energy of different water layer on graphene surface.

With multiple ice-like water layers on graphene coated surfaces, the adhesion energy $U_{SL}$ at the solid/liquid interface and the cohesive energy $U_{LV}/2$ at the liquid/liquid interface can be predicted by the DFT simulation$^1$, as shown in Fig. S3(a). By inputting these two physical quantities into the Young Dupre’s equation, as given by

$$\cos(\theta) = \frac{U_{SL} - U_{LV}/2}{U_{LV}/2} \tag{S1}$$
Where θ is the contact angle of macroscopic water droplet on solid surface. The DFT predicted contact angles of three different water structures on suspended graphene show 89.0° and 52.3° for OH-up and OH-down water structures, respectively, as summarized in Table S1. In comparison with the previous studies, the DFT predicted contact angle of OH-up ice-like water on suspended graphene agrees with that from molecular dynamics simulation results\textsuperscript{2}, and experimental static contact angle of 85°±5°\textsuperscript{3}.

Table S1. Summary of multiple ice-like water structures on suspended graphene

<table>
<thead>
<tr>
<th>Solid surface</th>
<th>Water molecules</th>
<th>$U_{SL}$ [KJ/mol]</th>
<th>$U_{LV}/2$ [KJ/mol]</th>
<th>DFT θ</th>
<th>Exp. θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended graphene</td>
<td>OH-UP</td>
<td>-6.28</td>
<td>-6.15</td>
<td>88.8°</td>
<td>85°±5°</td>
</tr>
<tr>
<td></td>
<td>OH-Down</td>
<td>-7.16</td>
<td>-4.3</td>
<td>48.3°</td>
<td></td>
</tr>
</tbody>
</table>
S.IV Time-resolved Fourier-transform infrared spectroscopy of fresh graphite flake surface

To find what kinds of adsorption on a fresh sample in ambient air, we performed time-resolved Fourier transform infrared spectroscopy (FTIR) on a fresh exfoliated graphite surface. Two major peak areas, corresponding 2800-2950 cm\(^{-1}\) and 3100-3600 cm\(^{-1}\), respectively, are observed in the single bond to hydrogen fingerprint region (2700-3600 cm\(^{-1}\)). In order to compare the FTIR spectra with different aging times, each measured spectrum was normalized by the most intense peak (~2950 cm\(^{-1}\)). The major peaks at 2850 cm\(^{-1}\) and 2950 cm\(^{-1}\) are recognized as C-H bonds stretching (Alkanes functional class), which is possibly airborne hydrocarbon contamination\(^4,5\). A broad peak area at 3100-3400 cm\(^{-1}\) corresponding to the O-H bonds stretching relatively increases as the aging time increases. The O-H bonds with the band center at 3250 cm\(^{-1}\) corresponds to the completed hydrogen bonding network of the ice-like water adlayer on graphite surface. Another peak, at 3350-3400 cm\(^{-1}\), on the shoulder of broad O-H band comes from the signal of liquid water\(^6\).
Fig. S4 Time-resolved Fourier-transform infrared spectroscopy of fresh graphite flake surface
S.V Transferred graphene on SiO$_2$/Si with and without annealing

The transferred graphene on SiO$_2$/Si substrate is annealed in vacuum at 200 °C for ten hours to see if the water contaminates at the interface between graphene and SiO$_2$ is removed. However, our experimental results of Raman spectroscopy show that after sample annealing, the water signal is still existed near 3380 cm$^{-1}$, as shown in Fig. S5(a). Meanwhile, the annealing may not be a good solution to obtain a clean interface in the transferred graphene samples because the defect is also created during the same process, as indicated by the Fig. S5(b).

Fig. S5. Raman spectra of graphene coated SiO$_2$/Si wafer with and without annealing 10-hours 200 °C in the spectra of the OH-bond region (a) and graphene defect peak region (b), respectively.

S.VI List of all used pseudo-potentials in Quantum Espresso package

When using QuantumEspresso, we took all pseudo-potentials from QuantumEspresso pseudopotential library. The used ultra-soft pseudo-potentials include C.pbe-n-rrkjus_psl.0.1.UPF, Cu.pbe-d-rrkjus.UPF, H.pbe-rrkjus_psl.0.1.UPF, O.pbe-n-rrkjus_psl.0.1.UPF, and Si.pbe-n-rrkjus_psl.0.1.UPF are used.
Reference


