# Study on the surface energy of graphene by contact angle measurements 

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## Supporting Document

Table S1. Contact angle data on HOPG presented as the average (standard deviation) of two tests.

|  | W | DIM | EG | G |
| :---: | :---: | :---: | :---: | :---: |
| Fresh | $64.6(2.9)$ | $20.6(1.6)$ | $43.3(1.4)$ | $35.8(0.6)$ |
| 1h air | $89.1(1.4)$ | $24.8(5.1)$ | $44.2(0.1)$ | $52.0(0.8)$ |
| 24h air | $97.0(1.8)$ | $38.2(1.1)$ | $60.3(5.9)$ | $74.5(4.9)$ |

Table S2. Surface free energy of HOPG determined by Neumann, Fowkes, and Owens-
Wendt models. Data presented as average (standard deviation).

| HOPG | Neumann model |  | Fowkes |  |  | Owens-Wendt |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\beta$ | $\begin{gathered} \gamma_{\mathrm{s}} \\ \left(\mathrm{~mJ} / \mathrm{m}^{2}\right) \\ \hline \end{gathered}$ | $\begin{gathered} \gamma_{\mathrm{s}}^{\mathrm{p}} \\ \left(\mathrm{~mJ} / \mathrm{m}^{2}\right) \end{gathered}$ | $\begin{gathered} \gamma_{\mathrm{s}}{ }^{\mathrm{d}} \\ \left(\mathrm{~mJ} / \mathrm{m}^{2}\right) \end{gathered}$ | $\begin{gathered} \gamma_{\mathrm{s}} \\ \left(\mathrm{~mJ} / \mathrm{m}^{2}\right) \\ \hline \end{gathered}$ | $\begin{gathered} \gamma_{\mathrm{s}}^{\mathrm{p}} \\ \left(\mathrm{~mJ} / \mathrm{m}^{2}\right) \end{gathered}$ | $\begin{gathered} \gamma_{\mathrm{s}}^{\mathrm{d}} \\ \left(\mathrm{~mJ} / \mathrm{m}^{2}\right) \end{gathered}$ | $\begin{gathered} \gamma_{\mathrm{s}} \\ \left(\mathrm{~mJ} / \mathrm{m}^{2}\right) \end{gathered}$ |
| Fresh | 0.00133270 | 60.2 | 7.8 | 47.6 | 55.4 | 8.1 | 43.5 | 51.6 |
|  | (0.00029094) | (0.9) | (2.7) | (0.5) | (3.2) | (2.5) | (1.6) | (0.9) |
| 1h | 0.00209292 | 57.1 | 0.5 | 46.2 | 46.7 | 0.8 | 50.4 | 51.2 |
| aged | (0.00011710) | (0.1) | (0.2) | (1.6) | (1.8) | (0.2) | (0.4) | (0.6) |
| 24h | 0.00152093 | 55.0 | 0.1 | 40.5 | 40.6 | 0.1 | 41.3 | 41.4 |
| aged | (0.00005682) | (0.3) | (0.1) | (0.5) | (0.7) | (0.2) | (1.3) | (1.5) |



Figure S1. Scanning electron micrograph of G/Cu sample.


Figure S2. AFM image of G/Cu sample. The ridge-like structure is due to the copper substrate.

Roughness measurements. Roughness of the G/Cu samples was determined by AFM to investigate its effect on the observed contact angle. At a scan size of $100 \times 100 \mu \mathrm{~m}$ and a resolution of $256 \times 256$, we obtained a projected surface area ( Ap ) of $10,000 ~ \mu \mathrm{~m}^{2}$ and an apparent surface area (Aa) of $10,009.5 \mu^{2}$. The roughness parameter for this sample was 1.00095 . Using the WCA of fresh and 24 h aged $\mathrm{G} / \mathrm{Cu}$, the Young's WCA was determined to be $50.9^{\circ}$ and $77.6^{\circ}$, respectively. This gives a difference between apparent and Young's WCA of $0.09 \%$ for the fresh surface and $0.02 \%$ for the aged surface.

Previous reports have shown that increasing the scan resolution concurrently increases the roughness parameter. To elucidate this effect on our samples, AFM scans were taken on the same $100 \times 100 \mu \mathrm{~m}^{2}$ area at $256,1024,2048$ resolution. We observed that the apparent surface area $\left(A_{a}\right)$ increased with resolution but its effect on roughness parameter was negligible. The roughness parameter was 1.0056 (1024 resolution) and 1.0257 (2048 resolution) which translates to a $\theta_{\mathrm{Y}}$ of $51.1^{\circ}$ (1024 resolution) and $52.0^{\circ}$ (2048 resolution) on fresh $\mathrm{G} / \mathrm{Cu}$.

The WCA of fresh flat $\mathrm{G} / \mathrm{Cu}$ was $56.3^{\circ} \pm 3.9^{\circ}$ and increased to $81.2^{\circ} \pm 1.4^{\circ}$ after 24 hours of air exposure. The flat $\mathrm{G} / \mathrm{Cu}$ was also characterized by AFM. The scan size was $99.83 \times 99.83 \mu \mathrm{~m}$ which gave a projected surface area $\left(A_{p}\right)$ of $9,966.1 \mu \mathrm{~m}^{2}$ and an apparent surface area $\left(A_{a}\right)$ of $9,968.0 \mu \mathrm{~m}^{2}$ at 256 resolution. This provides a roughness parameter of 1.00019 which translates to a Young’s WCA of $56.3^{\circ}$ and $81.2^{\circ}$ for fresh and 24 h aged surface, respectively. Scans at higher resolution yielded similar results.

