Supplementary Information

Measuring graphene adhesion using atomic force microscopy with a microsphere tip

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Note S1. Calculating Effective Coefficient λ for SiO$_2$ and Cu Substrate in Maugis-Dugdale Theory

AFM has been widely used to measure adhesion energy [S1,S2]. A general equation describing the relationship between adhesion force and adhesion energy is given by the Maugis-Dugdale theory

$$\gamma = \frac{F_{adh}}{\lambda \pi R} \tag{1}$$

where λ is the coefficient in a range of $1.5 \leq \lambda \leq 2.0$. Johnson-Kendall-Roberts (JKR) theory and Derjaguin-Muller-Toporov (DMT) theory describe the two extreme cases when $\lambda = 1.5$ and $\lambda = 2.0$, respectively. In the common intermediate systems, the transitional Maugis-Dugdale model between JKR and DMT needs to be employed. To determine the coefficient λ, Maugis defines a parameter μ to quantify the transition state

$$\mu = 1.157 \cdot \left(\frac{16 R \gamma^2}{9 K^2 z_0^3} \right)^{1/3} \tag{2}$$

where $0 < \mu < \infty$, with 0 and ∞ representing the DMT and JKR case, respectively, R is the tip curvature radius, γ is the adhesion energy per unit area, z_0 is the equilibrium separation between the surfaces, and K is the reduced elastic modulus of tip and sample defined as

$$K = \frac{4}{3} \cdot \frac{1}{(1-v_1^2)/E_1 + (1-v_2^2)/E_2} \tag{3}$$

where E_1 and E_2 are the tip and sample Young's moduli, and v_1 and v_2 are the tip and sample Poisson ratios, respectively. Since there is only one layer of carbon atoms on mica substrate, we used mica's Young's modulus and Poisson ratio as E_2 and v_2.

To solve the Maugis-Dugdale theory and calculate the coefficient λ in Eq. (1) directly, we used the empirical equations and a protocol proposed by Carpick et al. [S3] by fitting equations with a form between JKR and DMT equations. Similar equations were also obtained by Schwarz based on a physical model involving short and adjustable long-range interactions [S4]. The equations give a relationship between λ and μ as follows:

$$\lambda = -\frac{7}{4} + \frac{1}{4} \cdot \left(\frac{4.04 \cdot \mu^{1.4} - 1}{4.04 \cdot \mu^{1.4} + 1} \right) \tag{4}$$

The input parameters for SiO$_2$, Cu and mica are as follows: $E_{SiO2} = 70$ GPa, $v_{SiO2} = 0.3$; $E_{Cu} = 110$ GPa, $v_{Cu} = 0.36$; $E_{mica} = 178$ GPa, $v_{mica} = 0.25$. The equilibrium separation of the surfaces $z_0 = 0.30$ nm between graphene and SiO$_2$,[S5] and $z_0 = 0.36$ nm between graphene and Cu.[S6] After plugging the above parameters and the measured AFM pull-off force F_{adh}, Eqs. (1), (2) and (4) were solved self-consistently using a Matlab program. The resultant coefficients are $\lambda = 1.66$ for graphene on SiO$_2$ and $\lambda = 1.77$ for graphene on Cu.

Note S2. Accuracy Analysis of the Adhesion Measurement Method

In order to ensure an accurate measurement of adhesion energy via the AFM force spectroscopy method, pull-off instability should be prevented. To achieve that, adhesive force gradient between the spherical tip and graphene sample should be much larger than the cantilever's spring constant, whereas sufficiently lower than the contact stiffness.[S7] To verify the accuracy of our method and the variety of materials our method can apply to, we calculated these quantities for graphene/SiO$_2$ and graphene/Cu interfaces (as reported in the present work) as well as graphene/polystyrene (PS) interface to represent adhesion of graphene on dielectric, metal and polymer materials. For van der Waals interaction, the pairwise interaction between a carbon atom in graphene and an atom in the tip takes the form of Lennard-Jones potential, namely,

$$W_{LJ}(r) = -\frac{C_1}{r^6} + \frac{C_2}{r^{12}} \tag{5}$$

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Integrating Eq. (5) with respect to all the atoms gives rise to the interaction energy per unit area between graphene and tip, U_{vdW} [S8]

$$U_{vdW}(z) = -\gamma \left[\frac{3}{2} \left(\frac{z_0}{z} \right)^3 - \frac{1}{2} \left(\frac{z_0}{z} \right)^9 \right] \tag{6}$$

where z is the distance between the graphene and the spherical tip, z_0 is the equilibrium separation, and γ is the adhesion energy per unit area at z_0. Hence the van der Waals force per unit area g_{vdW} can be obtained by taking negative first derivative of U_{vdW} with respect to z

$$g_{vdW}(z) = -\frac{dU_{vdW}}{dz} = -\frac{9\gamma}{2z_0} \left[\left(\frac{z_0}{z} \right)^4 - \left(\frac{z_0}{z} \right)^{10} \right] \tag{7}$$

and the force gradient per unit area k_{vdW} is given by

$$k_{vdW}(z) = -\frac{d^2 U_{vdW}}{dz^2} = -\frac{27\gamma}{z_0^2} \left[-\frac{2}{3} \left(\frac{z_0}{z} \right)^5 + \frac{5}{3} \left(\frac{z_0}{z} \right)^{11} \right] \tag{8}$$

Note that force g_{vdW} in Eq. (7) reaches its minimum value (i.e., pull-off force) at the distance $z_{pull\text{-}off} = 1.165z_0$, where k_{vdW} equals zero. The force $F_{vdW}(z)$ as a function of separation distance z can be expressed as:

$$F_{vdW}(z) = \pi a^2 g_{vdW} \tag{9}$$

where a is the contact radius at pull-off. Applying Carpick's solution [S3] to the Maugis-Dugdale model, the contact radius a can be obtained from the following

$$a = \beta \cdot \left(\frac{\alpha}{1+\alpha} \right)^{2/3} \cdot \left(\frac{K}{\pi\gamma R^2} \right)^{-1/3}$$

$$\alpha = 0.98 \cdot \left(1 - e^{-1.082\mu} \right) \tag{10}$$

$$\beta = 1.54 + 0.279 \cdot \left(\frac{2.28 \cdot \mu^{1.3} - 1}{2.28 \cdot \mu^{1.3} + 1} \right)$$

where μ and K are defined in Eq. (2) and Eq. (3) respectively. The force $F_{vdW}(z)$ between graphene and SiO$_2$ or Cu tips is calculated by substituting the experimental data into Eqs. (7), (9) and (10). The force gradients in the range of $\pm$ 10% from the pull-off position are obtained as $0 < F_k < 723$ N/m and $0 < F_k < 807$ N/m for the graphene/SiO$_2$ and graphene/Cu interfaces, respectively.

As for the PS microsphere tip, we estimate its van der Waals adhesion energy with graphene per unit area γ_{ps} at equilibrium separation D by employing the traditional formula $\gamma_{ps} = H/12\pi D^2$,[S9] whereby the Hamaker constant H for PS and graphene is given as $H = 1.0$ eV,[S10] and the equilibrium separation between the surfaces $D = 0.3$ nm.[S11] The contact radius a_{ps} at pull-off for PS microsphere on graphene can be estimated to be $a_{ps} = 0.63 \cdot \left(6\pi\gamma_{ps}R^2/K_{ps}\right)^{1/3}$,[S9] where R is radius of the PS microsphere and K_{ps} is reduced elastic modulus of PS tip and substrate defined in Eq. (3). Substituting the above quantities into Eqs. (7) and (9), the force $F_{vdW}(z)$ as a function of separation z between graphene and PS tip is obtained. The force gradients in the range of $\pm$ 10% from the pull-off position is obtained as $0 < F_k < 136$ N/m for the graphene/PS interface.

The resultant $F_{vdW}(z)$ for graphene/SiO$_2$, graphene/Cu and graphene/PS are plotted in Fig. S1(a), (b) and (c) respectively. As a comparison, a straight dashed line at slope of the cantilever's spring constant 1.6 N/m is also plotted in the Fig. S1. Fig. S1 clearly shows that at the tangent point of the dashed line to the force curve, where pull-off takes place, the measured pull-off force is approximately equal to the maximum attractive force, i.e., the adhesion force.
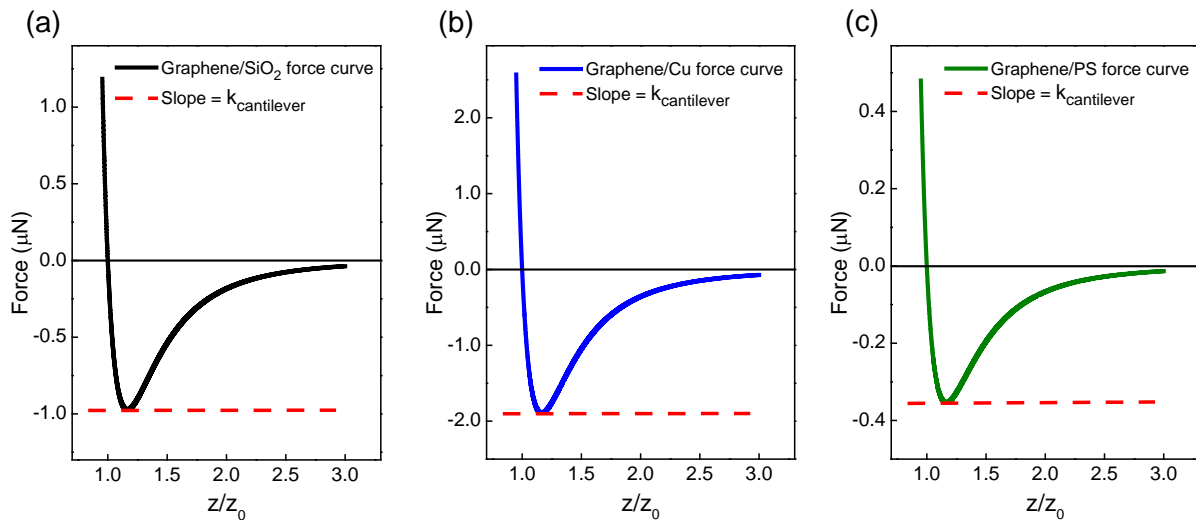

Fig. S1 Force curve (solid) between (a) SiO$_2$, (b) Cu, and (c) PS and graphene as a function of separation z/z_0. Plots are based on van der Waals interaction. The red dashed lines have slope of the cantilever's spring constant 1.6 N/m. The tangent point of the red dashed line to the force curve is the pull-off position. The plots show that the measured pull-off force is approximately equal to adhesion force – the maximum attractive force, for interaction of graphene/SiO$_2$, graphene/Cu and graphene/PS.

The contact stiffness C_k is estimated using the Hertzian contact equation [S12]

$$C_k = \frac{3}{2}Ka \qquad (11)$$

where K is the reduced elastic modulus of tip and sample defined in Eq. (3) and a is the contact radius. The calculated contact stiffness is $C_k = 1204$ N/m for graphene/SiO$_2$, $C_k = 1381$ N/m for graphene/Cu, and $C_k = 223$ N/m for graphene/PS, respectively. Thus it is validated that the contact stiffness is sufficiently larger than force gradient in pull-off area between graphene and all the three representative materials, which is required for the pull-off force to be a good measure of the adhesive force. Overall, the above analyses and calculations confirmed the accuracy of the present experimental method.

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