Origin of Hydration Lubrication of Zwitterions on Graphene

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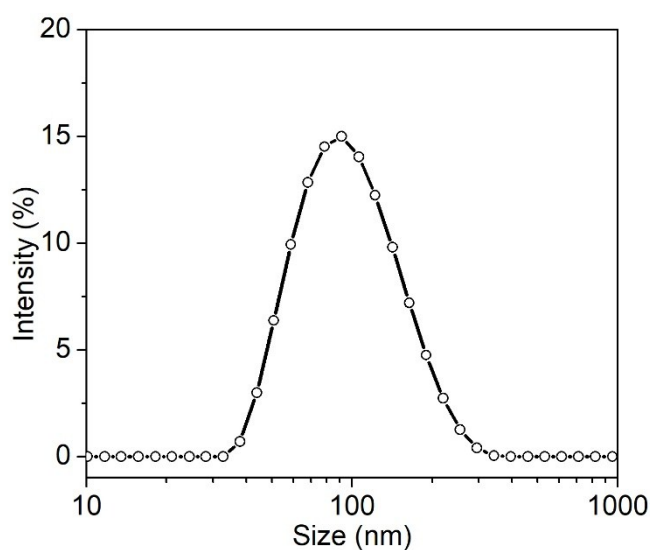1. Dynamic light scattering result of freshly prepared DSPC liposome

Figure S1 Dynamic light scattering result of freshly prepared DSPC liposome, showing the average diameter of single-unilamellar vesicle of 89 nm.

2. XPS data of the silica probe after rinsing in pure water (incubated overnight in the DSPC dispersion for adsorption in advance).
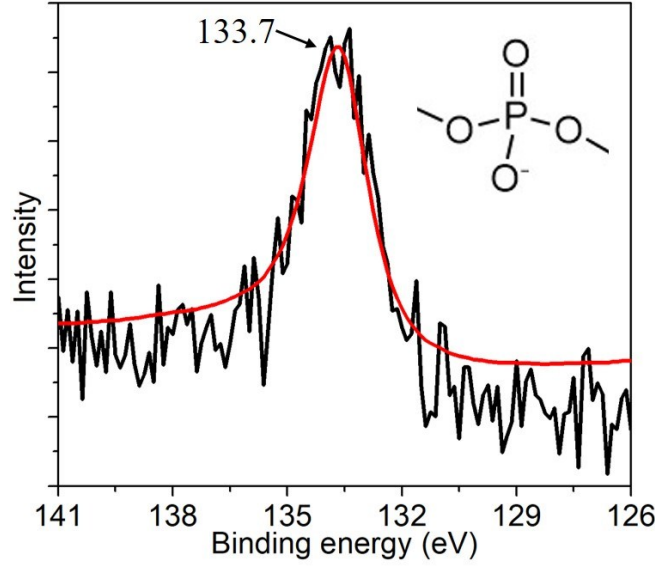
Figure S2　XPS data of the silica probe after rinsing in pure water, which was incubated overnight in the DSPC dispersion for adsorption in advance. It shows that there was a remarkable P 2p peak at the position of 133.7 eV, confirming that the DSPC molecules were successfully adsorbed on the probe.

3. Interaction energy between two plane parallel plates of unit area

When one surface is natural, and the other one has a constant charge with a low potential ($ze\psi_0/k_BT$ < 2), the repulsion potential energy for two planar surfaces is given by the following equation.[1]

$$E(D)=\frac{2nk_BT}{\kappa}\left[2y_0 ln\left(\frac{B+y_0\coth(\kappa D/2)}{1+y_0}\right)-\ln(y_0^2+\cosh\kappa D+B\sinh\kappa D)+\kappa D\right]-\frac{A_H}{12\pi D^2} \quad (S1)$$

where n is the number density of dissociated ions (in meters^{-3}), k_B is Bolzmann's constant (1.38×10^{-23}), T is the room temperature (298 K), κ^{-1} is the Debye screening length, D is the separation between the probe and graphene layer, A_H is the Hamaker constant, $y_0 = \frac{ze\psi_0}{k_BT}$, B$=\left[1+y_0^2\cos ech^2(\kappa D/2)\right]^{1/2}$, and $\psi_0=\frac{\psi_{01}+\psi_{02}}{2}$, where z is the valency of the cationic species, e is the electronic charge, ψ_{01} and ψ_{02} are the effective surface potentials of surfaces 1 and 2 at infinite separation.

4. Detailed discussion of the fitting procedure for normal force curve

Because the freshly cleaved graphene layer has a zero surface potential at far field, the parameter, y_0, in Equation S1 can be described by $y_0 = \dfrac{ze\psi_{SLB}}{2k_BT}$, where ψ_{SLB} is the effective surface potentials of surfaces SLB at infinite separation. The Hamaker constant of SLB is $A_{SLB} = 0.6\times10^{-20}\,J$,[2] and the Hamaker constant of graphene layer is $A_{gra} = 5\times10^{-20}\,J$.[3] Therefore, the Hamaker constant of SLB and graphene layer across pure water is about $A_H = \sqrt{A_{SLB}A_{gra}} = 1.73\times10^{-20}\,J$. Combined with Equation 1 and S1, there are two parameters, ψ_{SLB} and k^{-1}, which determine the normal force curve. Through the best fitting of the normal force curve (blue points) in Figure 2a with Equation 1 and S1, the values of the two parameters were obtained as $\psi_{SLB} = 99$ mV and $k^{-1} = 30.2$ nm. We also checked the value of $ze\psi_0/k_BT = 1.93$, which satisfied the pre-condition of Equation S1. The surface charge density of SLB was obtained by Equation S2.

$$\sigma_{SLB} = 2\left(2\varepsilon\varepsilon_0 k_B T n\right)^{1/2}\sinh(ez\psi_{SLB}/2k_BT) \tag{S2}$$

where ε is the dielectric constant of the solvent, ε_0 is the permittivity of the vacuum. Equation S2 gives the surface charge density of SLB as $\sigma_{SLB} = 0.064$ e/nm^2 (one charge per 15.6 nm^2). Our data clearly demonstrates that the interaction between SLB and graphene layer is repulsive and the repulsion originates from the compression of the double layer of the charged surface by the presence of the uncharged surface.

5. Effect of hydrodynamic drag on the frictional force

The hydrodynamic drag force (F_h) in shear direction can be described by Equation (S3).

$$F_h = 6\pi\eta vR \tag{S3}$$

where η is the viscosity ($\eta \approx 1$ mPas), v is the sliding speed, and R is the radius of colloidal probe (R

= 11.5 μm). Considering the maximal velocity (v_{max} = 30 μm/s) in Figure 3(c), we can get the maximal

hydrodynamic drag of F_{hmax} = 0.006 nN. Compared with the measured friction force in Figure 3, the

influence of hydrodynamic drag in shear direction is so little that it can be ignored. Therefore, the

flutter of AFM tip in pure water during the measurment can be ignored in our work.

6. Shear strength between the SLB and graphene layer as a function of velocity compared with the
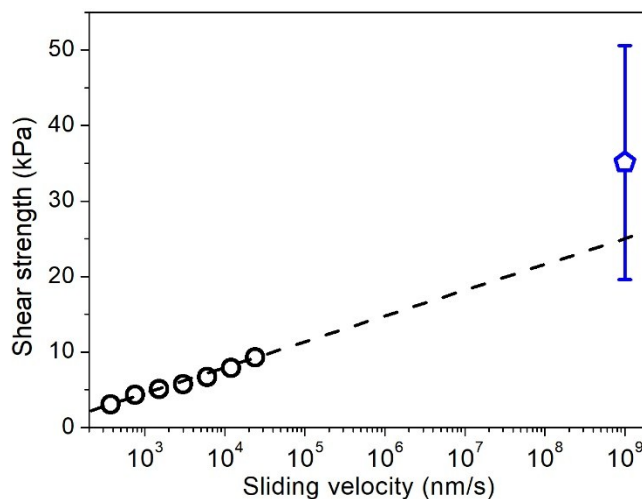
    simulated result.

Figure S3   Shear strength between SLB and graphene layer across pure water as a function of

velocity, obtained experimentally by $\tau = F_s/A$, where A is the contact area, F_s is the measured

frictional force under a normal load of 51 nN (Figure 3c). The blue point is the shear strength obtained

by MD simulation. We extrapolate the sliding velocity to 1.0 m/s and find that the measured shear

strength is 23.5 kPa at this velocity, which is just in the range of the simulated result.

Reference

(1) Gregory, J. Interaction of Unequal Double-Layers at Constant Charge. *J. Colloid Interface Sci.*

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(2) Attard, P.; Mitchell, D. J.; Ninham, B. W. The Attractive Forces between Polar Lipid Bilayers. *Biophysical Journal* **1988,** *53,* 457-460.

(3) Li, J. L.; Chun, J.; Wingreen, N. S.; Car, R.; Aksay, I. A.; Saville, D. A. Use of Dielectric Functions in the Theory of Dispersion Forces. *Phys. Rev. B* **2005,** *71*, 235412.