ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Interfacial Sliding and Buckling of Monolayer Graphene on a Stretchable Substrate

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Supporting Information

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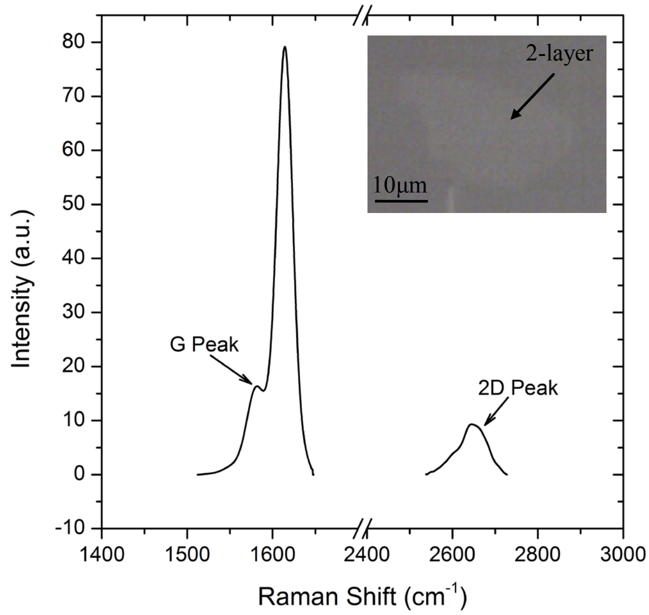

Figure S1. Raman spectrum of a bilayer graphene on PET. The large peak at 1615cm^{-1} is from PET background. Inset is an optical image of the graphene flake.

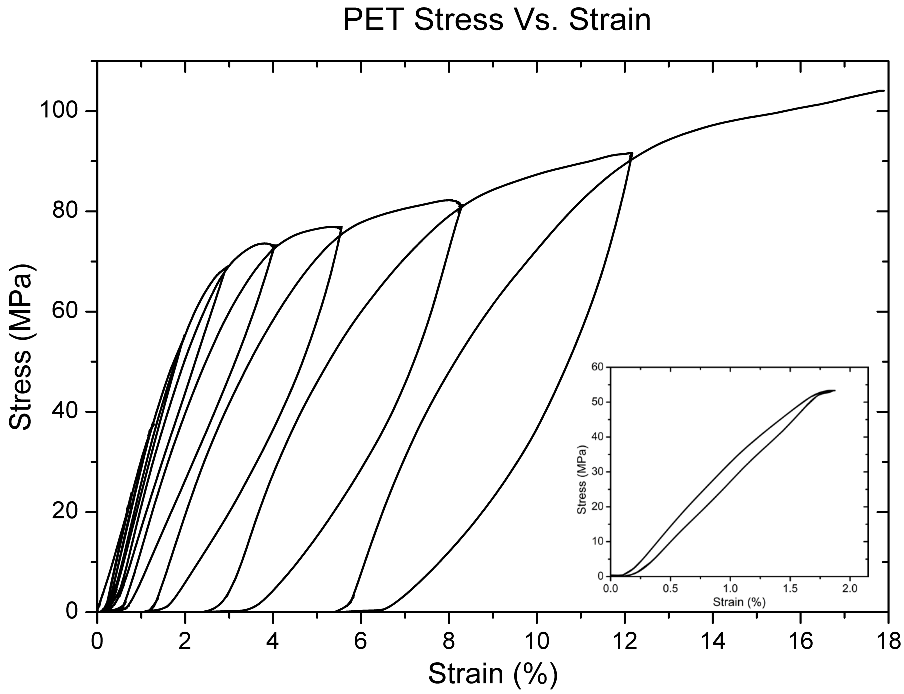

Figure S2. Nominal stress–strain curve of PET by uniaxial tension tests with cyclic loading and unloading for nominal strain up to 18% at strain rate of 0.001/s. Inset shows the stress–strain curve with strain less than 2.0%, for which the strain in PET was almost totally recovered after unloading. When the strain was larger than 2.0%, the strain was not fully recovered due to viscoplastic deformation. For example, when the PET was stretched up to 4% and 8%, the recovered strain was 3.3% and 4.8%, respectively.

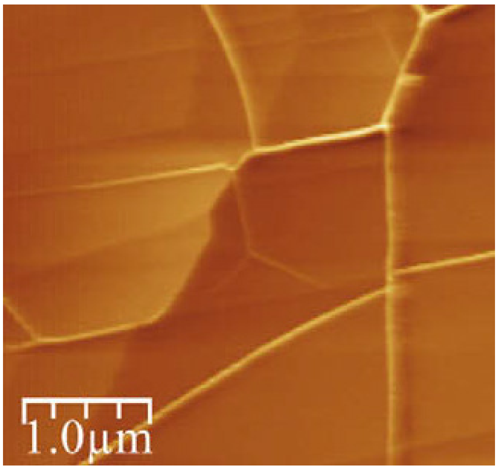

Figure S3. AFM image of a graphene synthesized by the SiC sublimation method.[1] The ridges are similar to those induced by stretching and releasing PET in the present study (see the AFM image in the last panel of Figure 4).

A Nonlinear Shear-Lag Analysis

Consider a graphene membrane of length L on an elastomer substrate. Apply uniaxial tension to the substrate. The graphene membrane first deforms concurrently with the substrate due to the interfacial shear stress transfer. When the interfacial shear stress reaches a critical value, however, the graphene may slide along the interface. Let τ be the interfacial shear stress and σ the axial force in the graphene membrane. The equilibrium requires that

$$\frac{d\sigma}{dx} = \tau \qquad \text{(S1)}$$

Assume the graphene membrane to be linear elastic so that

$$\sigma = E_{2D}\frac{du_g}{dx} \qquad \text{(S2)}$$

where u_g is the axial displacement of graphene and E_{2D} is the 2D Young's modulus of graphene. The axial strain in graphene is simply $\varepsilon_f = \sigma / E_{2D}$.

The substrate is subject to a nominal axial strain ε_m and the shear stress τ at the interface. The surface displacement of the substrate is approximately

$$u_m = \varepsilon_m x + \tau / k_m \qquad \text{(S3)}$$

where k_m is the effective surface stiffness of the elastomer (assumed to be a constant).

When ε_m is relatively small, there is no sliding between the graphene and substrate so that $u_g = u_m$ and

$$\sigma = E_{2D}\varepsilon_m + \frac{E_{2D}}{k_m}\frac{d\tau}{dx} \qquad \text{(S4)}$$

Substituting (S4) into (S1), we obtain

$$\frac{E_{2D}}{k_m}\frac{d^2\tau}{dx^2} = \tau \qquad \text{(S5)}$$

Solving (S5), we obtain

$$\tau = A\sinh(\beta x) + B\cosh(\beta x) \qquad \text{(S6)}$$

and

$$\sigma = E_{2D}\varepsilon_m + \left[A\cosh(\beta x) + B\sinh(\beta x)\right]/\beta \qquad \text{(S7)}$$

where $\beta = \sqrt{k_m / E_{2D}}$. To determine the coefficients A and B, we apply the boundary condition: the axial force σ must be zero at both ends of the graphene membrane. Let $x = 0$ at the center and $x = \pm L/2$ at the ends. The boundary condition requires that $B = 0$ and $A = -\frac{\beta E_{2D}\varepsilon_m}{\cosh(\beta L/2)}$. Therefore, the interfacial shear stress is

$$\tau(x) = -\beta E_{2D}\varepsilon_m \frac{\sinh(\beta x)}{\cosh(\beta L/2)} \qquad \text{(S8)}$$

And the axial strain in the graphene membrane is

$$\varepsilon_f(x) = \frac{\sigma}{E_{2D}} = \varepsilon_m\left[1 - \frac{\cosh(\beta x)}{\cosh(\beta L/2)}\right] \qquad \text{(S9)}$$

It can be shown that the maximum shear stress occurs at the ends of the graphene membrane ($x = \pm L/2$) with the magnitude

$$\tau_{\max} = \beta E_{2D}\varepsilon_m \tanh(\beta L/2) \qquad \text{(S10)}$$

When the maximum interfacial shear stress reaches a critical value ($\tau_{\max} = \tau_c$), interfacial sliding occurs between the graphene and the substrate. The critical strain for onset of sliding is thus

$$\varepsilon_c = \frac{\tau_c}{\beta E_{2D}}\coth(\beta L/2). \qquad \text{(S11)}$$

When $\varepsilon_m > \varepsilon_c$, the interface consists of two sliding zones emerging from the edges and a no-sliding zone in between. Noting the symmetry of the problem, let the sliding zone size to be s at each end. In the sliding zones ($L/2 > |x| > L/2 - s$), $u_g \neq u_m$ and the interfacial shear stress is assumed to be a constant ($\tau = \pm\tau_c$). By Eq. (S1), the axial force in graphene becomes

$$\sigma = \pm\tau_c(x \pm L/2) \qquad \text{(S12)}$$

In the no-sliding zone ($|x| < L/2 - s$), we have

$$\tau = A\sinh(\beta x) \qquad \text{(S13)}$$

$$\sigma = E_{2D}\varepsilon_m + A\cosh(\beta x)/\beta \qquad \text{(S14)}$$

By requiring the shear stress to be continuous at $x = \pm(L/2 - s)$, we obtain

$$A = -\frac{\tau_c}{\sinh[\beta(L/2 - s)]}.$$

By requiring the axial force in graphene to be continuous at $x = \pm(L/2 - s)$, we obtain an equation for the sliding zone size s:

$$\coth[\beta(L/2-s)]+\beta s=\frac{\beta E_{2D}\varepsilon_m}{\tau_c} \qquad \text{(S15)}$$

When $\varepsilon_m > \varepsilon_c$, we solve the equation (S15) to find the sliding zone size s, as shown in Figure S4.

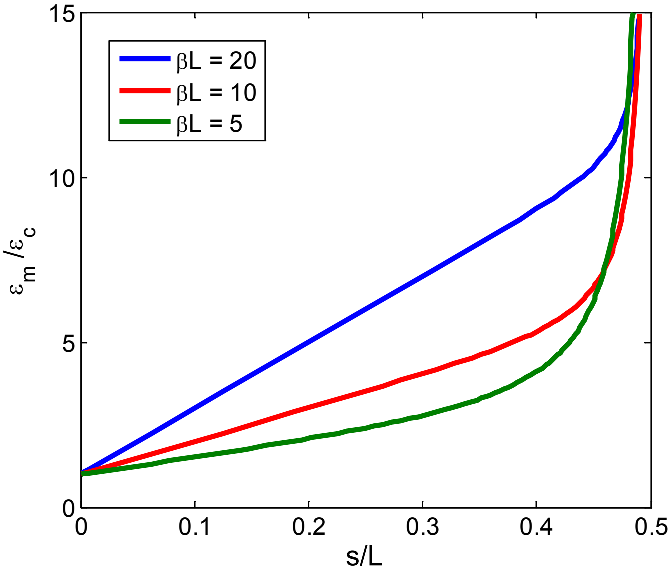

Figure S4. Normalized sliding zone size versus the applied strain.

Once s is known, the shear stress at the interface and the axial force in the graphene membrane can be calculated from Eqs. (S12)-(S14), as shown in Figure S5.

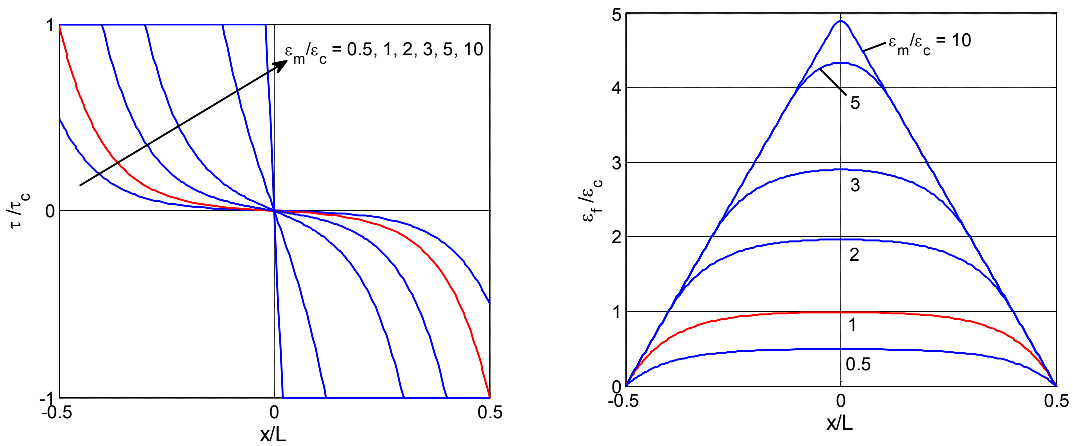

Figure S5. Evolution of the interfacial shear stress (left) and the graphene strain (right) as the applied suibstrate strain increases for βL = 10. Interfacial sliding begins when $\varepsilon_m/\varepsilon_c = 1$ (red).

Before sliding ($\varepsilon_m < \varepsilon_c$), the maximum axial strain in graphene at the center of the membrane (x = 0) is

$$\varepsilon_f(0)=\varepsilon_m\left[1-\frac{1}{\cosh(\beta L/2)}\right] \qquad \text{(S16)}$$

After sliding ($\varepsilon_m > \varepsilon_c$),

$$\varepsilon_f(0) = \varepsilon_m - \frac{\tau_c}{\beta E_{2D}} \frac{1}{\sinh[\beta(L/2 - s)]} \quad \text{(S17)}$$

Figure S6 shows the maximum membrane strain as a function of the applied strain, for different βL. It is noted that the strain in graphene approaches a plateau as observed in experiments, but the critical strain for onset of sliding (ε_c) does not correspond to the plateau. Instead, the plateau strain in the graphene membrane is approached as the sliding zone size (s) approaches $L/2$. In the limiting case when $s \to L/2$, the two sliding zones converge at the center, and the axial stress becomes linear on both side, with the maximum strain at the center approaching the limit, $\varepsilon_p = \frac{\tau_c L}{2E_{2D}}$.

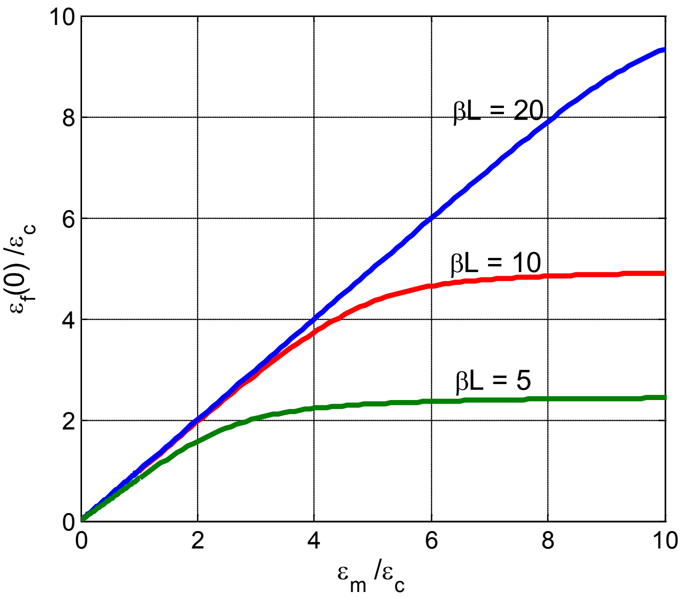

Figure S6. The maximum strain in graphene as a function of the applied strain, for different βL.

Next consider unloading (ε_m decreasing). During unloading, the sliding displacement first remains constant at each point while the shear stress relaxes. The governing equations can be written in the rate form:

$$\dot{\sigma} = E_{2D}\dot{\varepsilon}_m + \frac{E_{2D}}{k_m}\frac{d\dot{\tau}}{dx} \quad \text{(S18)}$$

$$\frac{E_{2D}}{k_m}\frac{d^2\dot{\tau}}{dx^2} = \dot{\tau} \quad \text{(S19)}$$

Solving the rate equations with the boundary conditions, $\dot{\tau} = 0$ at $x = 0$ and $\dot{\sigma} = 0$ at $x = \pm L/2$, we obtain that

$$\dot{\tau} = -\dot{\varepsilon}_m \sqrt{E_{2D}k_m} \frac{\sinh(\beta x)}{\cosh(\beta L/2)} \quad \text{and} \quad \dot{\sigma} = E_{2D}\dot{\varepsilon}_m \left[1 - \frac{\cosh(\beta x)}{\cosh(\beta L/2)}\right] \quad \text{(S20)}$$

The interfacial shear stress relaxes most rapidly at the edges and becomes zero when the substrate strain is unloaded by $\Delta\varepsilon_m = -\varepsilon_c$ (assuming that the maximum applied strain during loading is greater than the critical strain for onset of sliding). Further unloading leads to reverse shear stress and correspondingly compressive membrane strain in graphene near the edges. The reverse shear stress reaches the critical level when $\Delta\varepsilon_m = -2\varepsilon_c$, beyond which reverse sliding occurs.

Let s_r be the reverse sliding zone size. In the reverse sliding zone ($L/2 > |x| > L/2 - s_r$), $\frac{d\dot{\sigma}}{dx} = \dot{\tau} = 0$. Since $\sigma = 0$ at $x = \pm L/2$, $\dot{\sigma} = 0$ everywhere in the reverse sliding zone. For $|x| < L/2 - s_r$, the rate equations in (S18) and (S19) lead to

$$\dot{\tau} = -\dot{\varepsilon}_m \sqrt{E_{2D} k_m} \frac{\sinh(\beta x)}{\cosh(\beta L/2 - \beta s_r)} \quad \text{and} \quad \dot{\sigma} = E_{2D}\dot{\varepsilon}_m \left[1 - \frac{\cosh(\beta x)}{\cosh(\beta L/2 - \beta s_r)}\right] \text{(S21)}$$

Figure S7 shows the evolution of the shear stress and the membrane strain during unloading for βL = 10, after loading to $\varepsilon_m = 10\varepsilon_c$.

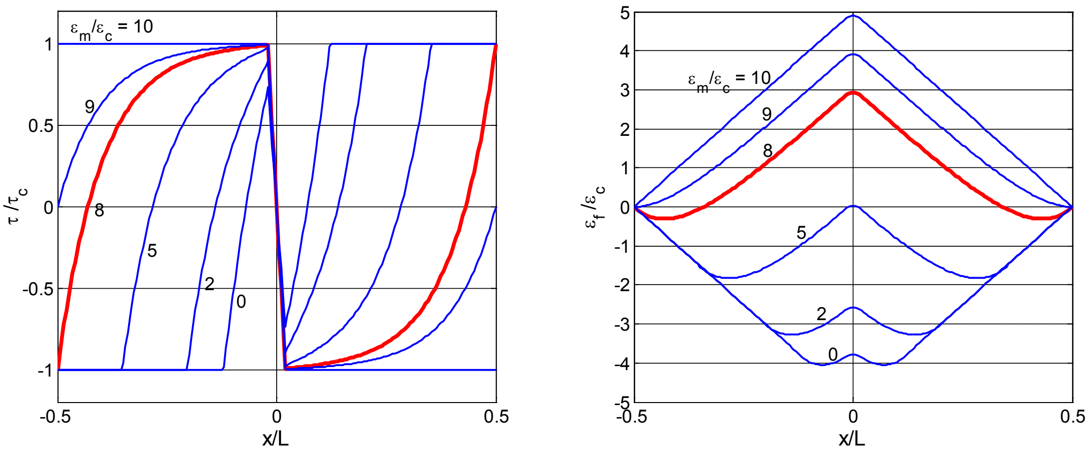

Figure S7. Evolution of the interfacial shear stress and the graphene strain during unloading for βL = 10. Unloading starts at $\varepsilon_m / \varepsilon_c = 10$, and reverse sliding begins when $\varepsilon_m / \varepsilon_c = 8$ (red).

To summarize the nonlinear shear lag analysis, we plot in Fig. S8 the membrane strain in graphene at the center, $\varepsilon_f(0)$, versus the applied substrate strain for a loading-unloading cycle with βL = 10. The hysteresis over the loading-unloading cycle is a result of the interfacial sliding. Note that the unloading leads to compressive stress/strain in the graphene membrane and may result in buckling. The shear-lag analysis assumes no buckling.

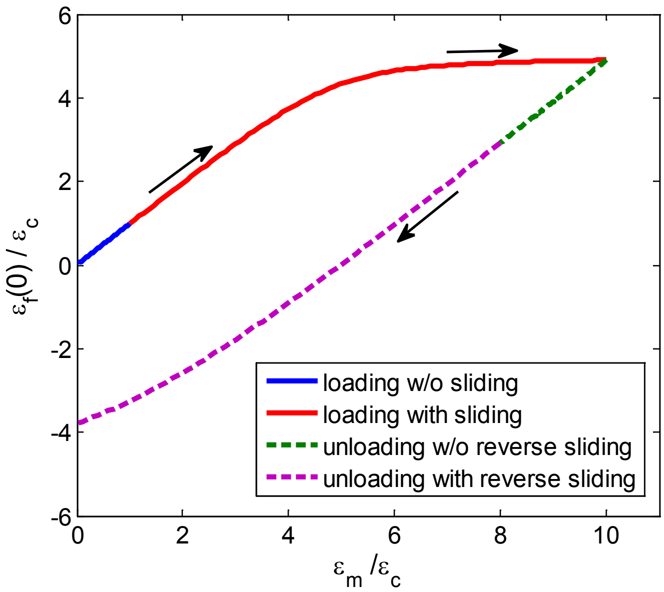

Figure S8. The membrane strain in graphene at the center, $\varepsilon_f(0)$, versus the applied substrate strain for a loading-unloading cycle with βL = 10, predicted by the nonlinear shear-lag analysis.

Supporting Information References

[1] G. Prakash, M. Capano, M. Bolen, D. Zemlyanou, R. Reifenberger, *Carbon* **2010**, 48, 2383.