

Manipulating and Controlling Graphene Adhesion

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Primary CNF Tools Used: E-beam evaporator; Oxford atomic layer deposition

Abstract:

We present a technique for patterning, measuring, and tuning surface energies between atomic layered materials and substrates under water. It is simple to implement, provides versatile, high precision measurements, and enables the development and engineering of adhesives at the nano scale. We use this technique to characterize the use of molecular pyrenes bound on glass, and optimize the pyrene density for maximum adhesion. Surface energy control immediately enables a graphene-transfer protocol that is resilient to adhesion failure under sonication. We further study the reproducibility and the hysteresis of adhesion and find a dramatic difference between peeling and re-adhesion that are insensitive to their timescales. More generally, our technique opens the door to a more complete and systematic approach to engineering stimuli-responsive adhesives and mechanical technologies at the nanoscale.

Summary of Research:

Figure 1A illustrates the fabrication sequence that results in lithographically defined patterns of distinct surface energies. Chemical modification using succinimidyl ester-terminated molecules yields release-layer-covered glass coverslips patterned with exposed glass surfaces functionalized by molecular glues (Figure 1B). Figure 1C shows an optical micrograph of five graphene/SU-8 cantilevers of varying widths, imaged in aqueous conditions in reflection mode. The force of adhesion can be directly measured by peeling the cantilever off the surface using a micromanipulator, as illustrated schematically in Figure 2A. We use interferometry to precisely determine the torque applied by the cantilever and the position of the interface between the bound and free regions of graphene.

Using energy conservation, the effective surface energy γ required for peeling can be calculated from the curvature κ in steady state and the Young's modulus E and thickness t of the SU-8 cantilever. For the data in Figure 2, this yields $\gamma_{\text{peel}} = 0.1 \text{ N/m}$. Figure 3 shows measurements of γ_{peel} for a variety of surfaces illustrated schematically in

Figure 3A, ranging from bare glass (very low adhesion) to a mix of pyrene and a diluent (maximal adhesion).

Finally, we explore the reproducibility and hysteresis of the peeling process (Figure 4).

Our technique led to the discovery of a dramatic difference of surface energy between peeling and re-adhesion. We further envision opportunities for switching adhesion properties by engineering adhesive molecules that change in response to optical, chemical, or thermal signals. In each of these cases, our experimental protocol can be readily adopted to provide the necessary information to tune, tailor, and design interfacial adhesives for atomically thin materials.

References:

- [1] Miskin, M. Z.; Sun, C. (co-first authors); Cohen, I.; Dichtel, W. R.; McEuen, P. L. Measuring and Manipulating the Adhesion of Graphene. *Nano Lett.* 2018, 18, 449-454.

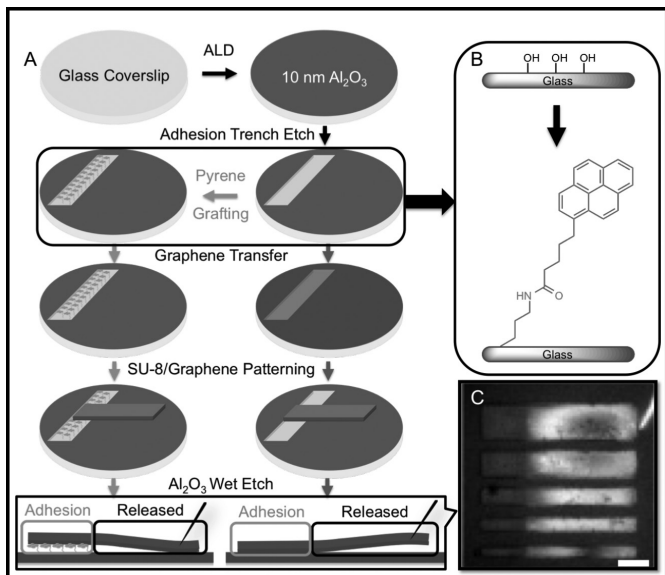


Figure 1: Controlled adhesion using pyrenes. A. Defining distinct patterns of surface energies between graphene and glass using lithography. B. Chemical functionalization on surface with bound, monolayer pyrenes. C. An optical micrograph of five graphene/SU-8 cantilevers bound by the patterned pyrene monolayer (left ends) after the Al_2O_3 release layer was removed.

Scale bar: 50 μm .

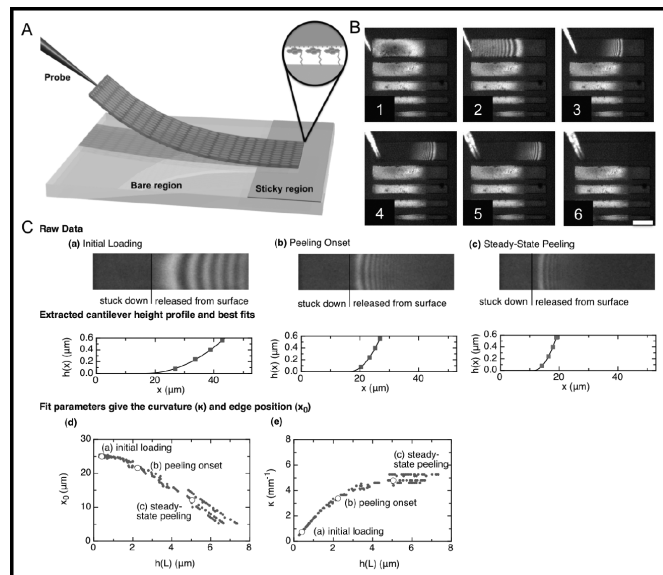


Figure 2: Peeling graphene. A. Loading a cantilever of monolayer graphene stiffened by SU-8 on top with a micromanipulator. The end of the cantilever is anchored on glass made sticky by surface-bound organic monolayers. The rest of the cantilever is released from the unfunctionalized glass surface. B. Reflection white-light micrograph series capturing the delamination of an anchored graphene cantilever. (Scale bar: 50 μm). All images have undergone linear contrast adjustment. C. Data analyses of peeling experiments: (a-c). Reflection white-light micrographs of a graphene/SU-8 cantilever at three stages of peeling: initial loading (a), peeling onset (b), and static-state peeling (c). Below each micrograph is their corresponding extracted cantilever height profiles and best fits. (d). A plot describing the change of lengths of a cantilever's bound portion as peeling progresses. The edge position x_0 is defined as the interface between the bound and the free portions of graphene, with respect to the left end of the cantilever. $h(L)$ describes the elevated height of the manipulator. (e). A plot describing the changes of the cantilever's radius of curvature as peeling progresses.

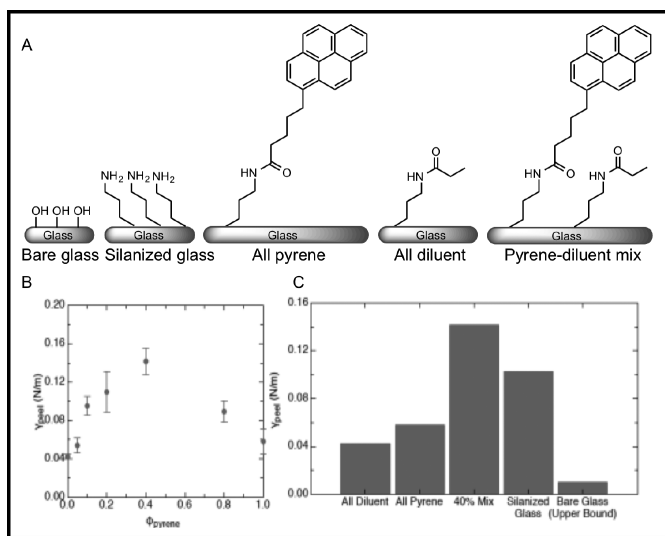


Figure 3: Optimizing adhesion using molecular adhesives. (A) Controlling surface energies using different surface organic monolayers. Surface-bound pyrene moieties serve as a molecular glue to enhance graphene adhesion. An acetyl-terminated moiety is used as a surface diluent to modulate the pyrene density. Amine-terminated moieties from direct glass silanization explore the adhesion enhancement via cation- π interactions. Bare glass is used as control. (B) Plot of graphene peeling measurements on surfaces treated with different pyrene loading% during surface adaptation. (C) Histogram of peeling surface energies on surfaces treated with all diluent loading, all pyrene loading, 40% pyrene loading, amine-terminated silanes, and bare glass.

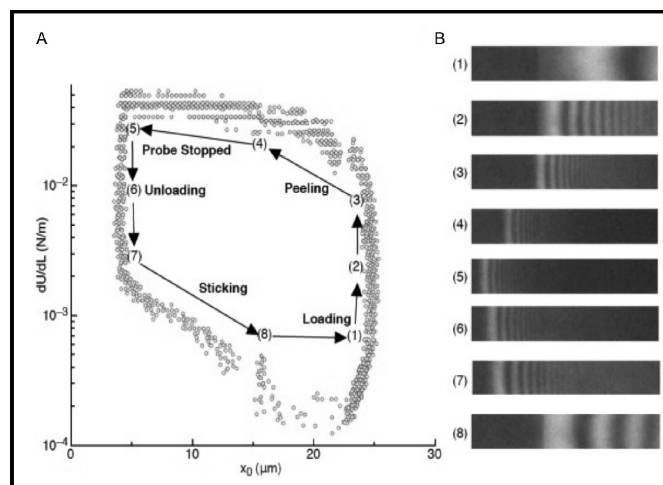


Figure 4: Reversibility and hysteresis of adhesion. A. A peeling-sticking cycle plotted by elastic energy changes per unit area (dU/dL) vs. the position of the peeling front with respect to the bound ends of the cantilever (x_0). B. Reflection white-light micrographs corresponding to different stages of the cycle.