

ACKNOWLEDGMENTS

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Preview

Harness the Power of Fracture: Controlled Fragmentation of Graphene via Substrate Necking

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Fracture has been a grave concern for practical applications of graphene and other atomically thin and brittle materials. By contrast, in this issue of *Matter*, Ming et al. present a method to harness the power of fracture in controlled fabrication of ordered graphene ribbons, which may initiate a new approach to making structures and devices based on two-dimensional (2D) materials.

As the very first and most prominent example of two-dimensional (2D) materials, graphene is the strongest material with a theoretical strength of 130 GPa.¹ However, from a fracture mechanics point of view, it is the fracture toughness that determines the actual strength of graphene given that crack-like flaws are inevitable in large-scale graphene samples. Recent experimental measurements have demonstrated that graphene suffers a very low fracture toughness, close to that of ideally brittle solids.² Moreover,

topological defects and flaws, such as dislocations, grain boundaries, triple junctions, holes, and notches, are commonly observed in large-scale graphene synthesized via chemical vapor deposition (CVD). The combination of brittleness and randomly distributed flaws makes fracture one of the most prominent concerns in large-scale applications of graphene. Many efforts have been devoted to understanding the fracture mechanics of graphene and how to toughen an atomically thin and brittle material.³ In compar-

son, advances on how to harness the power of fracture for controlled fragmentation of atomically thin materials remain rare.

Now, Ming et al.⁴ in this issue of *Matter* present a promising method of fabricating well-ordered graphene ribbons via controlled fragmentation of monolayer polycrystalline graphene (MPG). Adopting a thin film-substrate system, the researchers first transferred MPG onto a substrate of polycarbonate (PC), a thermoplastic polymer with an upturn in its stress-strain curve after initial yielding. Then, the authors applied uniaxial drawing to the PC substrate so that plastic deformation was localized in a necking zone and further spread out due to the hardening trend

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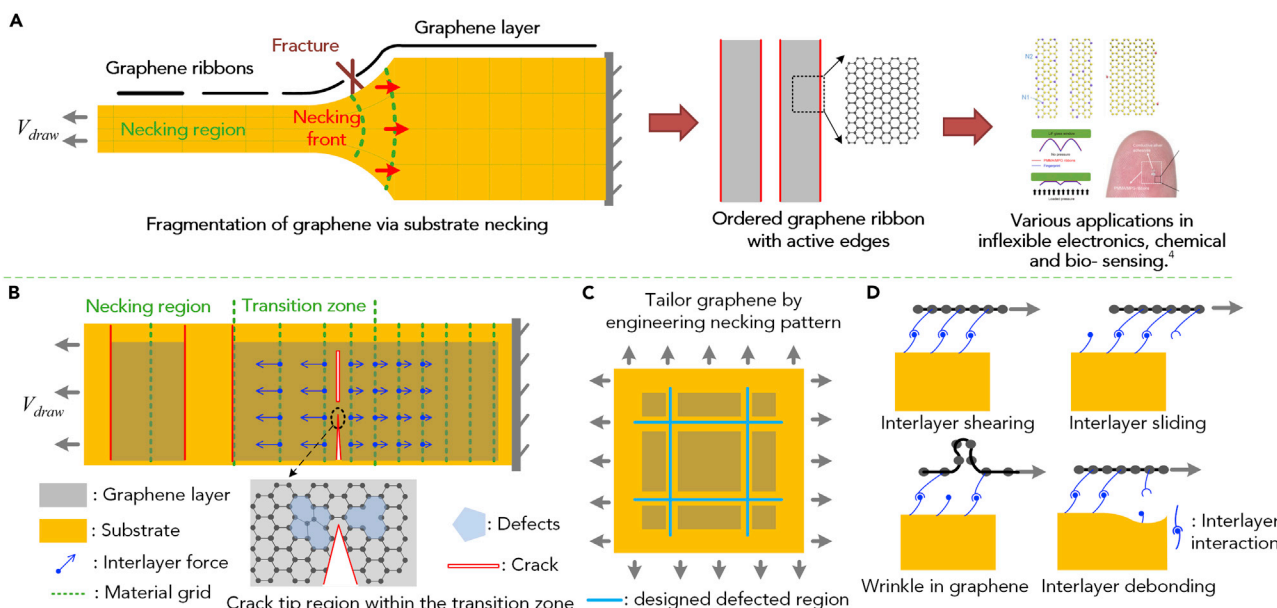


Figure 1. Controlled Fracture for the Fabrication of Ordered Graphene Ribbons via Substrate Necking

(A) A schematic of the fragmentation process of monolayer graphene on top of a propagating necking front in the substrate and the applications of the fabricated graphene ribbons, reprinted from Ming et al.⁴ (B) A fracture mechanics model of the crack field inside the necking front region, including the necking of the substrate, interlayer shearing or sliding, and brittle fracture of graphene. (C) Controlling the fragmentation patterns via engineering the distribution of necking in the substrate. (D) Engineering the in-plane fracture loading via tuning the interlayer interactions.

within the necking zone. Taking advantage of the sharp change of strain before and after the necking front, Ming and colleagues demonstrated that MPG was fragmented under interlayer interactions into a series of ordered submicron ribbons as the necking front propagated in the substrate. When comparing with the fragmentation patterns of MPG on substrates undergoing uniform deformation, the authors found that the crack pattern formed in this necking-assisted fracture process is well organized, robust, and insensitive to the randomly distributed atomic defects, grain orientations in the CVD MPG and the drawing speed. The fabricated graphene ribbons maintain high crystalline quality and show active edges, which may stimulate and enable promising applications in flexible electronics, chemical, and biological sensing (Figure 1A).

The controlled fragmentation of single-atom-thick graphene via substrate necking broadens the horizon of

applying fracture mechanics to thin film-substrate systems made of novel materials. As a long-time research topic, understanding and controlling fracture in thin film-substrate systems is of crucial importance in various engineering applications. Prominent examples include zirconia coatings as thermal barriers on superalloy in gas turbines, gallium nitride films as optoelectronic materials on sapphire substrate in light-emitting diodes,⁵ and solid electrolyte interphase (SEI) layer on silicon electrodes.⁶ In comparison with these examples, the substrate necking-assisted fragmentation of graphene pushes the frontier of fracture mechanics to a novel thin film-substrate system that involves an atomically thin and brittle film on a substrate designed to undergo a special type of material instability underloading. The interlayer interactions between graphene and the substrate potentially involve sticking, sliding, and even debonding. Surprisingly, in spite of these potential complications,

well-ordered crack patterns have been demonstrated in the presence of randomly distributed flaws and varying loading conditions.

The robustness and simplicity of this novel fabrication method imply not only promising applications in large-scale fabrication or processing of 2D materials, but also potential progresses in understanding fundamental knowledge about the interaction between non-uniform deformation of the substrate, fracture of the atomically thin film, and multi-stage interlayer interaction. Some of the open questions, opportunities, and potential research topics along this promising direction are listed below.

(1) Within the transition zone of the necking front, what is the crack tip field, and how does the fracture process interact with strain gradient in the substrate, interlayer interactions and preexisting defects within the graphene layer? In the demonstrated

fragmentation process, the repeated “cutting” process is attributed to the propagating necking front. Locally, inside this transition zone of the front, strain gradient is expected within the substrate. Because of the contrast of the deformation properties between graphene and the substrate, interlayer shearing, sliding or even debonding may occur asymmetrically before and after the front. Under such in-plane lateral loading, cracks initiate and propagate in a controlled path in graphene, almost insensitive to topological defects and crystalline orientation. To understand such a fracture process, a fracture mechanics model including the strain gradient of the substrate, sticking or sliding interlayer interactions, and the preexisting flaws inside the brittle graphene is in need (Figure 1B). With such a fracture mechanics model, a number of fundamental questions can be addressed. For example, what are the critical conditions of substrate strain gradient and interlayer interaction for crack initiation? How does the non-uniform interlayer shearing compete with preexisting defects in determining the crack initiation locations and propagation paths? What properties determine the periodicity of the crack pattern during the propagation of the necking front? What is the smallest size of the ribbon that can be fabricated via this necking-assistant fracture? Built on such basic understanding, the potential of generalizing this controlled fragmentation technique to engineer more sophisticated crack patterns may be further unveiled.

(2) Can we engineer the fragmentation patterns of graphene via designing the distribution of necking in the substrate? The selection of a thermo-plastic polymer substrate with a stably spreading necking zone is key to this fragmentation technique. In comparison with conventional shear-lag deformation modes in thin film-substrate or thin film-matrix systems undergoing

uniform deformation, the localized strain gradient at a necking front in the substrate not only helps define the crack paths, but also may open doors to possibilities of delicate engineering. For instance, by increasing the drawing speed over a critical value, multiple necking zones can be generated in a plastic material with strong hardening or stiffening after initial yielding.⁷ By prescribing defects in the substrate, such as locally reduced thickness, the locations of the necking zones may be controlled intentionally. Combining these engineering methods with the necking-assistant fracture technique, one may expect to tailor-cut graphene into designed geometries and dimensions mechanically (Figure 1C).

(3) Between 2D materials and the substrate, can we tune the interfacial interactions to affect the crack pattern and generalize this method to multilayer systems? The interface bonding between the substrate and 2D materials plays a crucial role in transferring the lateral loading from the substrate to the top layers. The nature of the interlayer bonding ranges from van der Waals (vdW) interaction between graphene and metal or polymer substrate⁸ to hydrogen bonding between graphene oxide sheets to covalent bonding between 2D material layers after nuclear irradiation or functionalization. Correspondingly, under lateral loading, various interlayer interactions can be triggered, including elastic interlayer shearing, finite interlayer sliding with repeated bond breaking and reformation, and interlayer debonding with the loss of the interaction (Figure 1D). The properties of these interactions, such as shear strength⁹ and interfacial fracture toughness,¹⁰ determine how much and in which way the shearing force is transmitted between the neighboring layers. By engineering the surface or interface properties, such as controlling the roughness of the substrate, wrinkles in the layers,

and chemical functionalization, various possibilities may exist to regulate and tune the in-plane shearing force through interlayer interactions. Combining these capabilities with the model of necking-assistant fracture, one may further push the limit of this controlled fragmentation process to multilayer 2D materials like vdW heterostructures and graphene oxide sheets.

In conclusion, by harnessing the power of substrate necking, interlayer shearing or sliding and brittle fracture of graphene, Ming et al.⁴ present a facile technique to fabricate well-ordered graphene ribbons through controlled fragmentation. Beneath the simplicity and robustness of this method, we anticipate promising opportunities for fundamental progress in the fracture mechanics of thin film-substrate systems as well as the fabrication and processing of many emerging 2D materials.

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Preview

Watching Water, Sodium, and Chloride Passing through a Graphitic Pore

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In this issue of *Matter*, Malmir and colleagues use sophisticated methods to give an atomic-scale view of saltwater permeation through a graphitic pore with high salt rejection. Na⁺ and Cl⁻ traverse the pore at different rates, leading to an electrostatic potential across the membrane.

Although reverse osmosis membranes for water desalination are established and considered a mature technology, the molecular control accessible with these synthetic membranes pales in comparison to biological ion-conducting trans-membrane proteins. Although the amazing properties of K⁺-channel proteins were known experimentally, the particular mechanisms that allow these properties were not understood until atomic-scale structures were obtained (in work that led to a Nobel Prize for Roderick MacKinnon).¹ If it is possible to understand the atomic-scale details of water and salt permeation through synthetic membranes, it may ultimately be possible to leverage this knowledge to broaden the conditions under which these membranes are useful. In this issue of *Matter*, Malmir et al. have taken a step in this direction by introducing methods that model permeation through an ultra-thin membrane in impressive detail.²

Analyzing permeation of saltwater through a membrane using atomistic

molecular simulations seems superficially simple, but the very limited time-scales imposed by molecular dynamics (MD)—on the order of nanoseconds to microseconds—place severe constraints on the number of molecular events that can be observed. This restricts the use of these methods in simulating stochastic dynamic events, such as ion permeation. The challenge is particularly acute for a membrane with a high level of salt rejection, because ions in the solution pass through the membrane orders of magnitude slower than water molecules. Malmir et al.² tackled this timescale challenge in two ways. First, they modeled a membrane of just three layers of graphite made porous by including a single sub-nm pore through the layers. Crudely, the flux through a membrane of thickness L scales as $1/L$, so the choice of an ultra-thin membrane maximizes this flux. By applying hydrostatic pressure in their MD simulations, Malmir et al.² were able to directly observe water permeation from a 1.5 M NaCl solution.

Second, they applied a sophisticated rare-event sampling technique (specifically, a method called jumpy forward-flux sampling) that gives accurate information on the permeation rates of Na⁺ and Cl⁻ ions. This approach gives direct information on the relation permeation rates and mechanisms of H₂O, Na⁺, and Cl⁻ through a graphite nanopore.

Malmir et al.'s² simulations show water fluxes that are in good agreement with predictions from the macroscopic Hagen-Poiseuille law. This is in contrast to earlier work that showed much higher water fluxes through membranes based on carbon nanotubes.³ Strong deviations from macroscopic predictions in carbon nanotubes occur because of the atomistic smoothness of the walls of these structures.⁴ The hydrogen-terminated pore simulated by Malmir et al.² does not share this smoothness. The estimated salt rejection of the simulated membrane is >99.99%, meaning that >10,000 water molecules pass through for every ion.

A more striking outcome from Malmir et al.'s² simulation is that Na⁺ and Cl⁻ traverse the membrane at very different rates. At a qualitative level, some differences in rates is to be expected because the size of the solvated ions, and hence their ability to enter and move through a sub-nm pore, differ.

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