Nanoscale fracture in graphene

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ABSTRACT

Fracture of a monolayer graphene is governed by the competition between bond breaking and bond rotation at a crack tip. Using atomistic reaction pathway calculations, we identify a kinetically favorable fracture path that features an alternating sequence of bond rotation and bond breaking. Our results suggest that the mechanical cracking can create fracture edges with nanoscale morphologies due to the non-uniform bond deformation and rupture induced by the localized high stresses near the crack tip. Such fractured edges may provide a structural basis of tailoring the electronic properties of graphene either intrinsically or by further edge functionalization.

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The Griffith load is given by
\[ \frac{K_G}{\sigma} = \sqrt{2\gamma c}, \]
where \( \gamma \) is the surface energy density that can be determined by the equilibrium bond energy and the lattice constant. The BOP4S potential gives \( K_{G1} = 6.460 \text{ eV Å}^{-5/2} \), where the subscript ‘1’ denotes the first step of crack extension by one atomic spacing, as shown in Fig. 2 (from a to b). In addition to the theoretical prediction, the Griffith load can also be determined numerically by finding the critical applied load that is less than 0.05 eV Å. A continuous MEP is generated by polynomial fitting of the discrete MEP [33]. The energy barriers for bond rotation are consistently 1–2 eV lower than those for bond breaking. This indicates that bond rotation is more energetically and kinetically favorable. A similar trend has been recently observed in silicon [19]. In the MEP calculations, we treat the nucleation of two SW defects as a sequential rather than a simultaneous barrier-crossing process since the former is more kinetically favorable. Fig. 2e shows the energy barriers at various K-loads. The energy barriers for bond rotation are consistently 1–2 eV lower than those for bond breaking. This indicates that bond rotation is more kinetically favorable. The activation energy barrier for bond rotation is about 10.3 eV Å^{-5/2}, identified as the athermal load for instantaneous bond rotation.

We have investigated the fracture of graphene beyond the first step of formation of two SW defects. Due to the presence of the SW defects, the mechanical environment local to the crack tip is considerably altered. The bond rotations significantly relax both von Mises effective shear stress and the hydrostatic stress at the crack tip (see Supplementary data). The relaxed stress field suppresses further bond breaking and rotation by increasing energy barriers and lowering the thermodynamic driving force. As a result, the Griffith load of crack extension for the SW defect-present configuration (Fig. 2c) is markedly higher than that for the dislocation-absent configuration (Fig. 2a) due to the shielding effect of defects at the crack tip. We numerically determine the Griffith load by invoking the energy balance criterion as illustrated earlier, yielding \( K_{G2} = 10.114 \text{ eV Å}^{-5/2} \) for the configuration shown in Fig. 2c, where the subscript ‘2’ denotes the second step of crack extension by one atomic spacing.

Starting from the configuration shown in Fig. 2c, we have studied several kinetically possible processes, e.g., bond breaking, bond rotation-induced emission of 5/7 dislocations, and bond rotation-induced separation between the pentagon and heptagon. Here we focus on the bond breaking modes which are more kinetically

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1 For interpretation of colour in Fig. 1, the reader is referred to the web version of this article.
favorable, including symmetric cleavage fracture by breaking the first bond at the crack tip (Fig. 3a to b), and asymmetric cleavage fracture by breaking the bond adjacent to the first bond at the crack tip (Fig. 3a to c). In Fig. 3d and e, we plot, respectively, the corresponding load-dependent formation energies and kinetic barriers. Fig. 3e shows that there exists a crossover point of the applied load of the two bond breaking processes, denoted by $K^{\text{cross}}$. The crossover of energy barriers implies the switching of the rate-limiting step. When $K^{\text{app}} < K^{\text{cross}}$, asymmetric bond breaking is more kinetically favorable; when $K^{\text{app}} > K^{\text{cross}}$, symmetric bond breaking will dominate kinetically.

Taking either Fig. 3b or c as the starting configuration, we have further investigated the crack extension pathways, as shown in Fig. 4. For clarity, Fig. 4a and b, respectively, duplicate Figs. 2a, c, and 4c, c', respectively, corresponds to Fig. 3b and c. For the configuration in Fig. 4c, our NEB calculations show that a further bond rotation is kinetically favorable as compared to bond breaking. The bond rotation leads to the separation of the pentagon and the heptagon, and moves the heptagon toward the crack tip, see Fig. 4d. This configuration is geometrically similar to Fig. 4b except that the pentagon is moved away from the crack tip. The subsequent crack-tip response would be bond breaking, similar to the

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**Fig. 2.** Competing processes of crack-tip bond breaking and bond rotation. (a $\rightarrow$ b) Crack extension by breaking a crack-tip bond (in blue). (a $\rightarrow$ c) The brown-colored bonds are rotated by 90°, forming the 5/7 SW defect residing on each side of the crack surfaces. (d) The minimum energy paths of the two competing mechanisms at the Griffith load. (e) Load-dependent activation energy barriers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 3.** Crack-tip bond breaking after the first step of bond rotation. (a) Crack tip after the first step of bond rotation. (b) Symmetric and (c) asymmetric bond breaking. (d) Load-dependent formation energies and (e) activation energy barriers from the NEB calculations.
process from configuration (b) to (c). Overall, for the symmetric bond breaking process, the crack propagates by the alternating sequence of bond breaking and bond rotation in a self-similar manner, as shown in Fig. 4: \(a \rightarrow b \rightarrow c \rightarrow d \rightarrow b \rightarrow c \rightarrow d\). This sequence repeats, leading to macroscopic fracture.

Taking Fig. 3d (i.e., Fig. 4c’) as the starting configuration, our NEB calculations show that one of the bonds that belongs to the large open rings is prone to breaking, see Fig. 4d’. This causes a local shift of the fracture path downward by one hexagon. The shifted crack tip is enclosed by perfect hexagons, and it is geometrically similar to Fig. 4a. Therefore, further crack extension would proceed by alternating sequence of bond breaking and bond rotation in a self-similar manner, as shown in Fig. 4: \(a \rightarrow b \rightarrow c' \rightarrow d' \rightarrow a\). Because of the structural and loading symmetries, this asymmetric breaking mode can also occur by shifting the crack path upward. During a kinetic crack-growth process under quasi-static loading [34] the two pathways revealed in Fig. 4 are both kinetically possible. The overall crack extension path is expected to remain straight, as dictated by the condition of quasi-static crack growth on the plane of maximum normal stress. As a consequence, the alternating sequence of bond breaking and bond rotation can create the fracture edges with mixed five- and seven-membered rings, and the asymmetric bond breaking can lead to the atomic-scale roughness of fracture edges. Of course, the dynamic effect in a fast fracture could cause crack kinking or branching, beyond the scope of this research [35].

In conclusion, we show that the fracture of a monolayer graphene can involve an alternating sequence of bond rotation and bond breaking under the quasi-static loadings around the Griffith limit of fracture. Such a fracture mode is kinetically preferred, as verified by using different interatomic potential models. However, it requires a further study using the first-principles modeling, and more importantly, through fracture experiment with high-resolution imaging. The fracture of graphene can be further manipulated by imposing mixed modes of far-field loading, including in-plane and out-of-plane shear. The mechanical cracking of graphene can create the unique atomic-scale morphologies of fracture edges fundamentally because of the non-uniform bond deformation and rupture at the crack tip with localized high stresses. This non-uniformity may open up an opportunity to create reconstructed edges that provide a structural basis of tailoring the electronic properties of graphene, either intrinsically or through further edge functionalization.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2010.05.090.

References