Oxygen-Driven Unzipping of Graphitic Materials

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Optical microscope images of graphite oxide (GO) reveal the occurrence of fault lines resulting from the oxidative processes. The fault lines and cracks of GO are also responsible for their much smaller size compared with the starting graphite materials. We propose an unzipping mechanism to explain the formation of cracks on GO and cutting of carbon nanotubes in an oxidizing acid. GO unzipping is initiated by the strain generated by the cooperative alignment of epoxy groups on a carbon lattice. We employ two small GO platelets to show that through the binding of a new epoxy group or the hopping of a nearby existing epoxy group, the unzipping process can be continued during the oxidative process of graphite. The same epoxy group binding pattern is also likely to be present in an oxidized carbon nanotube and cause its breakup.

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Carbon based materials play a significant role in nanoscience and nanotechnology applications. Fullerenes, nanotubes, and 2D graphite platelets are the building blocks for nanoelectronic devices [1], chemical and biosensors [2,3], drug delivery applications [4], hydrogen-storage systems [5], quantum wires [6], and nanocomposites [7,8]. Fabrication and manipulation of these building blocks involves both new physics and new technology. Oxidation is one of the basic processes used to manipulate carbon materials as in the case of carbon nanotube cutting [9]. Similarly, graphite oxide (GO) is an important intermediate in the process of graphite exfoliation to produce very thin graphitic flakes that in some cases consist of a single atomic layer [10]. It is relatively well known how oxygen can be incorporated into a graphene layer: oxidation results in functionalization by epoxy and hydroxyl groups. The extensive literature on the chemistry of graphite oxidation has provided information on average substitution levels, the varieties of oxygen species, and reaction conditions [11–13]. Yet, surprisingly little has been done to connect oxidation chemistry to the morphology of the graphene sheets, except for the layer spacing during intercalation and curved graphitic structure caused by topological or vacancy defects in the carbon lattice. Intriguingly, we have observed cracks in GO that are directly related to the oxidation process. However, the processes that lead to crack formation in GO and carbon nanotube cutting are not known at the atomistic level. Here we find that cracks are the result of a cooperative effect that leads to unzipping. Using first-principles quantum mechanical calculations we elucidate the origin of the reaction mechanism that causes ordered oxidation and subsequent unzipping and cracking. This result was unanticipated by the previous purely "mean field" chemical understanding of graphite oxidation.

Under a well-controlled oxidization process, we examined the dark field optical microscope images of GO produced by the Staudenmaier method [14] which reveals the occurrence of fault lines not observed in the starting graphite material (Fig. 1). It is also known that oxidation of single-wall carbon nanotubes is an effective method to chemically cut and shorten their lengths [9]. A basic question thus arises: how can such a fracture occur upon oxidation? By utilizing a density-functional theory (DFT) approach, we aim to investigate the low level oxidation processes occurring on a graphene sheet and identify those reactions that could lead to cracks. This is of importance to the molecular control of distribution and location of the oxygenated functional groups [15]. In addition, understanding the energetics that drives the unzipping process is indispensable for finely tuned fabrication and engineering of the graphite composites at the nanolength scale.

In this Letter we propose a model of GO unzipping initiated by the formation of epoxy groups on the graphite surface. During the oxidative process on a graphene sheet,

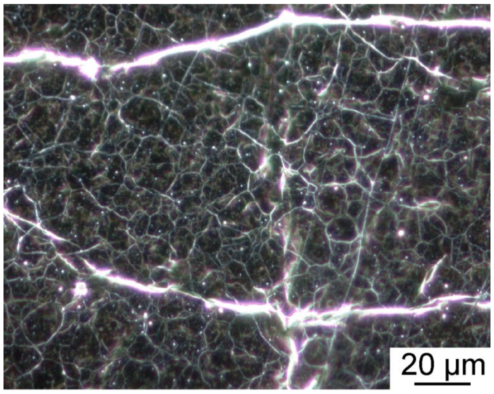

FIG. 1 (color online). During oxidization of graphite, a marked decrease in size is observed. An optical microscope image of partially oxidized highly oriented pyrolytic graphite (HOPG) shows line defects (fault lines). The same defects are not observed on freshly cleaved HOPG.

we assert that once two epoxides are formed on the opposite ends of a hexagon, there is a strong tendency for GO to form more "open epoxide rings" along a straight line. On the basis of the strain generated by the cooperative alignment of epoxy groups, we introduce a mechanism which accounts for the initiation of crack formation on GO [16]. In contrast, hydroxyl groups do not bind cooperatively on graphite and therefore probably do not participate in the unzipping process of GO.

In a first-order approximation, GO can be viewed as a hexagonal carbon lattice to which various oxygen-containing functional groups are randomly attached. In the following, we employ two small planar fused benzene ring compounds, $C_{12}H_{24}$ (coronene) and $C_{54}H_{12}$, as our theoretical models to study oxidative processes. Upon oxidation, both compounds possess aromatic regions and aliphatic six-membered rings, similar to a bulk GO. The stoichiometry varies with the preparation methods and the distribution of functional groups is presumably irregular. Unlike a previous theoretical study of GO [17] where oxygen sites were placed as far as possible from each other on a graphitic sheet, we attached one to four epoxy groups to $C_{12}H_{24}$ and $C_{54}H_{12}$ in various configurations where epoxy groups are next to each other, and then relaxed the structure until the force on any individual atom was less than 0.01 eV/Å within DFT.

When a single oxygen atom binds to a graphitic area of the GO surface, an epoxy group is formed by joining two adjacent carbon atoms with a single bond. Such a three-membered epoxide ring, shown on the left of Fig. 2, is severely strained. This is because the two carbon atoms need to undergo configuration changes from a planar sp^2-hybridized to a distorted sp^3-hybridized geometry. During the formation of a single isolated epoxy group, Fig. 4(a), the total energy of the system is lowered by ~2.4 eV. At the same time, the C-C bond is stretched from 1.42 Å (pristine carbon lattice) to 1.58 Å (a single epoxy group). As illustrated on the right of Fig. 2, if the C-C bond was not constrained by the rigid carbon network around it, a further relaxation of the three-membered epoxide ring would open up and break the C-C bond with the energetic gain from the released strain.

To investigate the interaction between nearby epoxy groups, we have carried out calculations with several randomly oxidized graphite oxide platelets. Because the experimental conditions are usually such that only one side of the graphene sheet is accessible to the chemical reactions, we focus here on the oxygens attached to the same side of the sheet. Upon examination of the energetics of these differently oxidized carbon sheets, it becomes clear that a special clustering can result from formation of two or more epoxy rings. We first consider nearest neighbor epoxide-epoxide interactions. Two epoxy groups cannot bind to the same carbon atom since the bonding geometry would exceed the maximum valence bonds a carbon can form. Within the same hexagonal ring, two possible binding patterns are juxtaposed in Fig. 3. When two epoxy groups bind to the opposite ends, the binding of one epoxy group increases the binding of the other. This is due to the conformational change induced by the cooperative unzipping by the two oppositely placed epoxy groups. Overall, among a few dozens of configurations we studied, only those with linearly aligned epoxy groups yield unzipped structures, as shown in Fig. 4(b)–4(d).

In an oxidized coronene molecule with two epoxy groups, the total energy of the unzipped configuration [Fig. 4(b)] is lower than any other configurations by about ~1.2 eV. In a larger model system, $C_{54}H_{12}$, we also found that the oxidized C-C bonds can not remain intact under the concerted strain caused by linearly aligned epoxy rings which form a fault line [Figs. 4(c) and 4(d)]. Comparing to the strained epoxy ring (Fig. 2, left), each unzipped epoxy ring (Fig. 2, right) gains an additional energy ~1 eV in oxidized coronenes and $C_{54}H_{12}$.

Having considered the behavior of a single hexagonal ring upon oxidation, we know that if epoxy groups are aligned in a straight line, the underlying C-C bonds will break and give rise to a fault line or cracks. The question that remains to be answered is how the epoxy groups could arrange themselves in a linear clustering pattern. During the oxidative process of GO, a further unzipping process can happen via two routes, (1) the binding of a new epoxy group (with the oxygen provided by the environment), or (2) migration of other existing epoxy group on GO to the designated location. The oxidative process of GO is often realized by treating graphite with strong oxidizing agents, for example, in a solution of $KMnO_4$ in H_2SO_4 [11]. While under such conditions oxygen can (and will) bind to most accessible sites, the attack of the carbons with an oxygen nearby is most favorable. Figure 5 shows the energetic change when an oxygen binds to a location which results

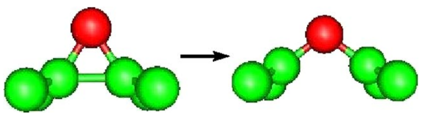

FIG. 2 (color online). An epoxy group stretches the underlying C-C bond. On the left, with a single epoxy group, the C-C bond length is 1.58 Å. On the right, when 2 or more epoxy groups are aligned in a line and induce unzipping, the C-C bond breaks and their distance increases to ~2.3 Å.

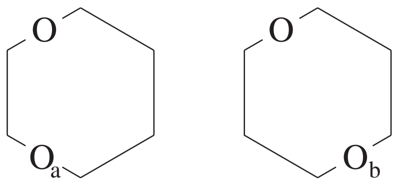

FIG. 3. Two epoxy groups can attach to the same side (left) or the opposite ends (right) of a hexagonal ring.

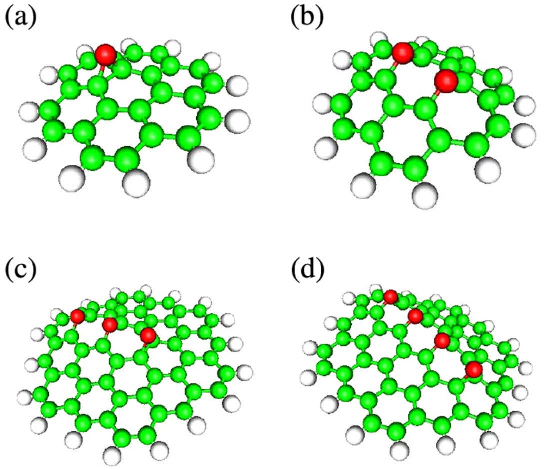

FIG. 4 (color online). (a) One epoxy group is attached to a coronene molecule. (b) Two epoxy groups are aligned on a coronene molecule which initiate an unzipping process. (c) Three epoxy groups are aligned on a piece of graphene. (d) Four epoxy groups aligned on a piece of graphene. The graphene platelet shows a crack.

in two broken epoxy groups. The energy gain (5.5 eV) is much larger than the formation of an isolated epoxy group (2.4 eV). Next, once an epoxy group binds to a carbon lattice, is it stationary or does it have limited mobility to move to a new site? To answer this question, we performed a first-principles string based reaction path optimization [18] to compute the energy barrier of an epoxy group hopping between adjacent sites. The calculation finds the minimum energy pathway connecting two metastable states of a system, which in our case was a graphene platelet with an epoxy group, $C_{54}H_{18}O$, as shown in Fig. 6. The hopping barrier for an isolated epoxy group is found to be ~0.9 eV at the DFT level. Although the energy barrier is substantial [19], it may be significantly reduced in aqueous solutions in which GO was prepared. If an isolated epoxy group on GO have limited mobility (especially in the locally hot region due to the oxidative process in acidic solutions), when it hops to the unzipping prone site (O_b in Fig. 3), the released strain energy will then "lock" the epoxy group into this site and extend the existing unzipping.

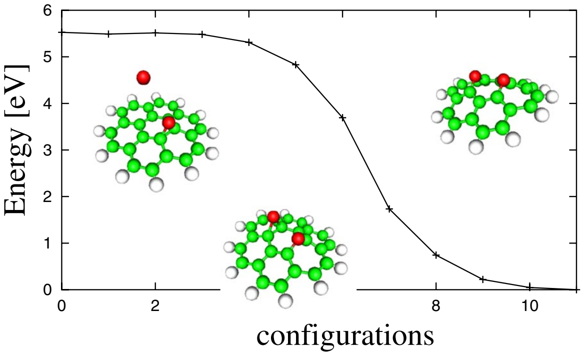

FIG. 5 (color online). Energetic change during the binding of a free oxygen to an oxidized coronene molecule. Three configurations are shown: the initial configuration (left), an intermediate configuration (middle), and the final configuration (right). Note that both C-C bonds of the epoxy groups are broken in the final product.

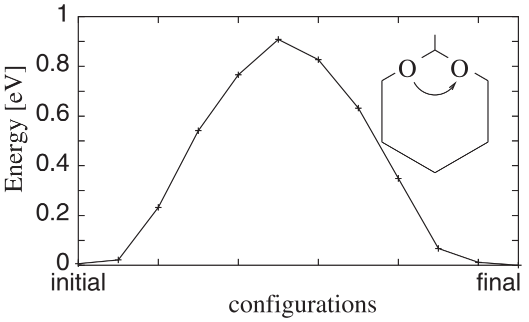

FIG. 6. The energy barrier for an epoxy group moves on a graphene platelet ($C_{54}H_{18}$). The hopping barrier is ~0.9 eV.

To illustrate the locking of an epoxy group at an unzipping prone site, we compute two different minimum energy pathways for the hopping process. Figure 7 shows that the energy barrier is smaller for the unzipping process (path 2), and due to the locking (most energetically favorable), the hopping of an epoxy group to the unzipped prone position is highly irreversible.

Among advances in the chemical manipulation of carbon nanotubes, fluorization [20] and oxidation [9] have been shown to be effective methods to chemically cut (or shortening) single-wall carbon nanotubes (SWCNT). Similarly, direct sidewall functionalization of multiwall carbon nanotubes can be carried out in dilute acidic solutions, where oxidation proceeds invasively from the outer

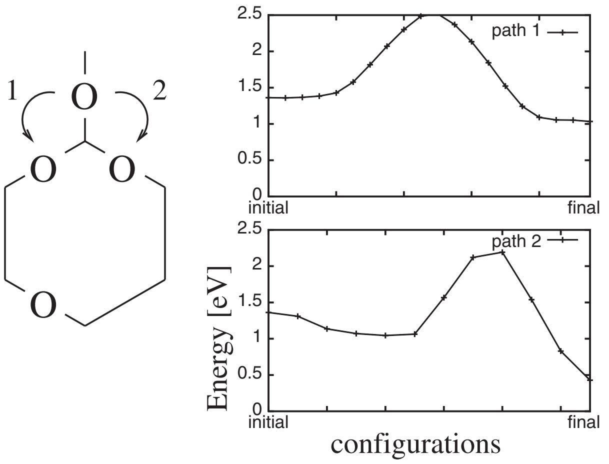

FIG. 7. Minimum energy pathways of an epoxy group moving on an oxidized coronene molecule. The most stable configuration is when the two epoxy groups bind to the opposite ends of a hexagonal ring, which is used as a reference to compare energies between path 1 and path 2. Path 1 has an energy barrier of 1.1 eV while path 2 has a lower energy barrier of 0.83 eV.

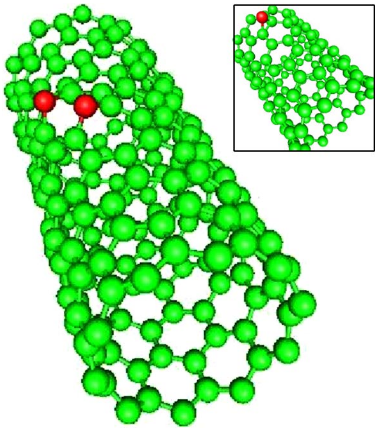

FIG. 8 (color online). Two epoxy groups create a small crack on a SWCNT. Inset: a single epoxy group does not break the attached C-C bond.

to the inner graphitic layers [21]. The unzipping process described above results in linearly serial breaking of C-C bonds, so the mechanism can be easily realized for the circumferential direction of a carbon nanotube and account for its breaking.

Figure 8 shows a [10, 0] SWCNT with one or two epoxy groups attached to it. When an epoxy group binds to the SWCNT, the underlying C-C bond is stretched from 1.4 to 1.5 Å, similar to the case of graphene sheets. When two epoxy groups bind to the opposite ends of a hexagonal carbon ring, the underlying C-C bonds can not sustain the concerted stretch and break. Note that this is in striking contrast with *fluorinated* nanotubes where even a high density of attached fluorines leaves the carbon network mostly intact [22,23]. The binding energy profile of epoxy groups on a SWCNT is similar to that on graphite: when two epoxy groups are well separated, their binding energies are additive; on the other hand, if two epoxy groups bind cooperatively, the system gains an additional energy ~1 eV from the released strain energy in C-C bonds. This suggests that the unzipping mechanism may also be responsible for breaking of oxidized CNTs [9].

In this work we have proposed a mechanism to explain the observed fault lines and cracks on GO. It is shown that strain generated by the cooperative alignment of epoxy groups can initiate cracks on GO. The continuation of unzipping processes can be achieved by binding of a new epoxy group during the oxidation or hopping of an existing epoxy group and subsequent locking. Given that an open epoxy ring is substantially weaker than a closed ring, our work gives insight into chemical shortening of carbon nanotubes via oxidative processes.

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[1] A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekkerdagger, Science **294**, 1317 (2001).
[2] L. Valentini, I. Armentano, J.M. Kenny, C. Cantalini, L. Lozzi, and S. Santucci, Appl. Phys. Lett. **82**, 961 (2003).
[3] R.J. Chen, S. Bangsaruntip, K.A. Drouvalakisdagger, N.W.S. Kam, M. Shim, Y. Li, W. Kim, P.J. Utzdagger, and H. Dai, Proc. Natl. Acad. Sci. U.S.A. **100**, 4984 (2003).
[4] C.R. Martin and P. Kohli, Nat. Rev. Drug Discov. **2**, 29 (2003).
[5] S.H. Joo, S.J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, and R. Ryoo, Nature (London) **412**, 169 (2001).
[6] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, and C. Dekker, Nature (London) **386**, 474 (1997).
[7] L.C. Brinson *et al.* (to be published).
[8] A.A. Mamedov, N.A. Kotov, M. Prato, D.M. Guldi, J.P. Wicksted, and A. Hirsch, Nat. Mater. **1**, 190 (2002).
[9] J. Liu *et al.*, Science **280**, 1253 (1998).
[10] H.C. Schniepp, J.-L. Li, M.J. McAllister, H. Sai, M. Herrera-Alonso, D.H. Adamson, R.K. Prud'homme, R. Car, D.A. Saville, and I.A. Aksay, J. Phys. Chem. B, **110**, 8535 (2006).
[11] A. Lerf, H. He, M. Forster, and J. Klinowski, J. Phys. Chem. B **102**, 4477 (1998).
[12] A. Hirsch and O. Vostrowsky, Top. Curr. Chem. **245**, 193 (2005).
[13] A.B. Bourlinos, D. Gournis, D. Petridis, T. Szabó, A. Szeri, and I. Dékány, Langmuir **19**, 6050 (2003).
[14] L. Staudenmaier, Ber. Dtsch. Chem. Ges. **31**, 1481 (1898).
[15] S. Banerjee and S.S. Wong, J. Phys. Chem. B **106**, 12 144 (2002).
[16] Depending on the way the tensile stress is relieved, a thin film made of multiple layers may crack or buckle. See Ref. [10].
[17] A. Incze, A. Pasturel, and P. Peyla, Phys. Rev. B **70**, 212103 (2004).
[18] Y. Kanai, A. Tilocca, A. Selloni, and R. Car, J. Chem. Phys. **121**, 3359 (2004).
[19] The hopping of an epoxy group has a comparable energy barrier as single vacancy diffusion in graphite [G.D. Lee *et al.*, Phys. Rev. Lett. **95**, 205501 (2005)]. Based on a quick estimate of the fast stretching mode of C-C bonds, the hopping rate of an epoxy group on graphite is roughly once every 100 sec at room temperature.
[20] Z. Gu, H. Peng, R.H. Hauge, R.E. Smalley, and J.L. Margrave, Nano Lett. **2**, 1009 (2002).
[21] K.C. Park, T. Hayashi, H. Tomiyasu, M. Endo, and M.S. Dresselhaus, J. Mater. Chem. **15**, 407 (2005).
[22] K.N. Kudin, H.F. Bettinger, and G.E. Scuseria, Phys. Rev. B **63**, 045413 (2001).
[23] K.N. Kudin, G.E. Scuseria, and B.I. Yakobson, Phys. Rev. B **64**, 235406 (2001).