Observation of Microscale Superlubricity in Graphite

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(Received 25 September 2011; revised manuscript received 19 December 2011; published 15 May 2012)

Upon shearing a microscale lithographically defined graphite mesa, the sheared section retracts spontaneously to minimize interface energy. Here, we demonstrate a sixfold symmetry of the self-retraction and provide a first experimental estimate of the frictional force involved, as direct evidence that the self-retraction is due to superlubricity, where ultralow friction occurs between incommensurate surfaces. The effect is remarkable because it occurs reproducibly under ambient conditions and over a contact area of up to 10×10 μm^2, more than 7 orders of magnitude larger than previous scanning-probe-based studies of superlubricity in graphite. By analyzing the sheared interface, we show how the grain structure of highly oriented pyrolitic graphite determines the probability of self-retraction. Our results demonstrate that such self-retraction provides a novel probe of superlubricity, and the robustness of the phenomenon opens the way for practical applications of superlubricity in micromechanical systems.

DOI: 10.1103/PhysRevLett.108.205503 PACS numbers: 62.20.Qp, 46.55.+d, 68.35.Gy

Friction and wear are crucial parameters in micromechanical systems featuring sliding components, due to the large surface-to-volume ratio in such small systems [1–3]. As a result, the past decade has seen increasing research interest in superlubricity, a phenomenon first proposed by Hirano *et al.* [4,5], where the friction force almost vanishes between two solid surfaces. The effect occurs when there is structural incommensuration between two crystalline solid surfaces, typically due to a relative rotation of their lattices, leading to the systematic cancelling out of the friction force on the atomic scale.

To date, all experimental evidence of structural superlubricity was obtained on the nanoscale and under vacuum or ultrahigh vacuum [6–14]. It was supposed that, "for sufficiently large contacts, superlubricity might break down, as the two lattices are not perfectly rigid, and a network of misfit dislocations should form between the two, the motion of which will dissipate energy" [7]. It is worth noting that ultralow friction was observed in mm-sized graphite intercalated with C60 molecules [14,15]; despite that, it is not due to the structural superlubricity discussed in this Letter. Even at the nanoscale, actuating controlled superlubric motion typically requires cumbersome experimental setups and complex sample preparation [6–8,10,12–14]. In addition, both experiments and simulations showed that such structural superlubricity on the nanoscale can be easily suppressed by various mechanisms [11,12]; for example, if the sliding surfaces are unconstrained, they will twist spontaneously to a more stable commensurate configuration, resulting in lock-in to a much higher friction state [12].

In this Letter, we report a new way to probe superlubricity using lithographically defined square mesas of highly oriented pyrolytic graphite (HOPG) that are 200–400 nm high and up to 20 μm in edge length. For this system, we show the first direct evidence that superlubric motion can be actuated by shearing the mesa and releasing the resulting sheared flake of graphite. The effect occurs reproducibly and even under ambient conditions. We also provide important insights into how the polycrystalline structure of HOPG on the microscopic scale enables the superlubric motion. This new way of probing superlubricity overcomes several barriers to practical applications of this intriguing phenomenon.

Fabrication of the microscopic graphite mesas has been described in Ref. [16], following a method proposed in Ref. [17]. As sketched in Fig. 1(a), square graphite mesas capped with SiO_2 and with linear dimensions 1.0–20.0 μm and thicknesses 200–400 nm are fabricated from HOPG (Veeco, ZYH grade). The mesa samples are then transferred into a scanning electron microscope (SEM, FEI Quanta 200F) or an optical microscope (OM, HiRox KH-3000) equipped with a micromanipulator MM3A (Kleindiek). Graphite flakes are sheared from the mesas using a tungsten microtip in contact with the SiO_2 cap of the mesa [Fig. 1(b)].

When the sheared flakes are released, some of them spontaneously return to their original positions on the mesas [Fig. 1(c)], to minimize surface free energy. Those that exhibit self-retraction do so reproducibly, with the smallest flakes showing the highest self-retraction probability [16]. For 1.0 μm mesas, self-retraction occurs for

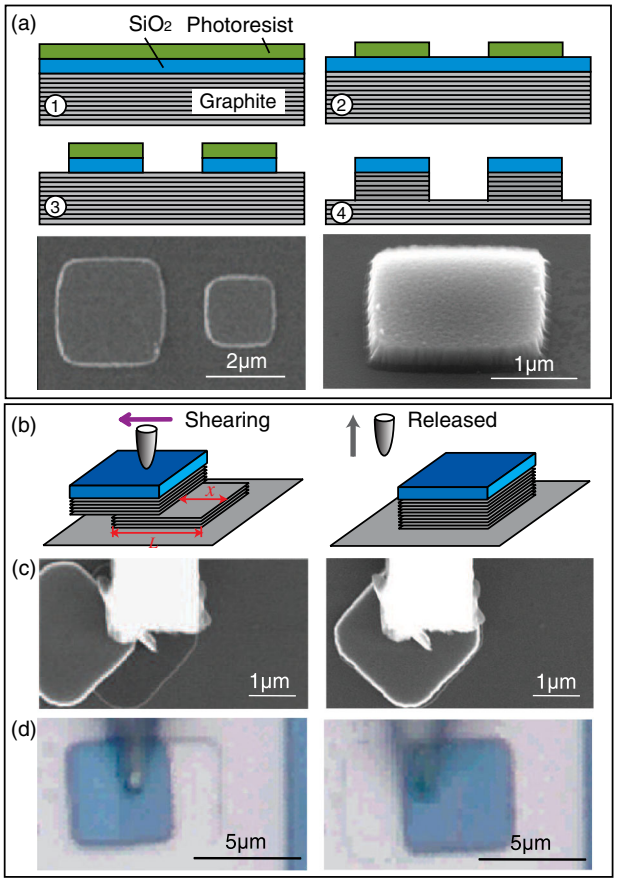

FIG. 1 (color online). (a) After mechanical exfoliation, (1) a silicon dioxide (SiO_2) film is grown on the graphite surface by plasma-enhanced chemical vapor deposition, and the film is coated with photoresist. (2),(3) Microscopic SiO_2 squares are defined by electron beam lithography and (4) used as a mask for reactive ion etching of the squares into the HOPG, to define graphite mesas. SEM images of the top and side views of the mesas are shown. (b) Illustration of a mesa being partially sheared with a micromanipulator, to form a self-retracting flake on a graphite platform. When the microtip is raised to release the flake, it automatically returns to its original position on the mesa. (c) Observation of this process in a vacuum in a SEM. (d) Observation of the same process under ambient conditions with an optical microscope.

100% out of a population of 20 studied. The self-retraction probability is 58% and 12% out of a population of 20–60 studied for 1.7 μm and 10.0 μm mesas, respectively. For mesa sizes >20.0 μm, no self-retraction is observed. The speed of self-retraction is greater than the frame rate of the SEM or optical video imaging, and we estimate from high-speed camera video that it is greater than 1 mm/s. Similar self-retraction was observed in multiwalled carbon nanotubes [18–20] and proposed as a means to create GHz mechanical oscillators [21].

Shearing a flake from a square graphite mesa of edge length L to a distance x creates new surfaces of total area $2Lx$ [Fig. 1(b)] and thus an excess surface free energy of $U = 2\gamma Lx$, where γ is the graphite basal plane surface energy which is estimated to be about 0.1–0.2 J/m^2 [21,22]. The corresponding self-retraction force is thus $F_{\text{retract}} = |-dU/dx| = 2\gamma L$. The friction resistance force is $F_f = \tau_f L(L - x)$, where τ_f is the shear strength [23]. Since the flake self-retracts, we can conclude that this force overcomes the friction at the interface. So, we obtain an upper bound estimate of the areal friction stress as $\tau_f^{\text{upper}} = 2\gamma/(L - x_{\max})$, where $x_{\max}$ is the maximum sheared distance in our experiments, typically <5 μm for a 10 μm mesa. This analysis yields the upper bound estimate $\tau_f^{\text{upper}} \approx 0.02$–$0.04$ MPa. In the friction force microscopy (FFM) measurements, the frictional force in the superlubric state was nearly zero [7]. FFM does not allow such accurate estimation, but, based on the estimated contact area in those measurements of about 1.9 nm^2 and a force resolution of 15 pN of the FFM, the superlubricity friction stress should be 0 ± 7.5 MPa [7,10], which, within the large uncertainty, is compatible to our results.

Direct measurement of basal plane friction shear strength of single crystalline graphite (with commensurate interlayer contact) has been measured by Dienwiebel *et al.* in their FFM experiments to be $\tau_s = 0.1$ GPa [7]. This is 3 orders of magnitude larger than the above estimate for τ_f, suggesting that, when graphite is in a commensurate orientation, motion due to the self-retraction force should be strongly suppressed. To confirm this, we performed a series of experiments where we used the tungsten microtip to deliberately rotate the sheared flake before releasing it. These measurements were repeated for flakes with edge lengths of 1.0–5.0 μm and typical thicknesses of 200–400 nm.

We have carried out over 70 rotation events for one sample with edge length of 2 μm prepared under high vacuum conditions in SEM. What we observe is a set of lock-in states (13 events) at certain rotation angles, with a clear 60° symmetry, as illustrated in Fig. 2 (and Supplemental Movie 1 [24]). The self-retraction occurs in other directions, which are continuously distributed between the lock-in directions. The self-retraction at a given rotation angle is observed to be reproducible. Detailed statistics are available in the Supplemental Material (SM) [24]. Similar results are found for other samples observed in a SEM and an optical microscope.

These observations demonstrate that the self-retraction effect depends sensitively on the atomic geometries of the contacted surfaces, excluding explanations based on contamination or a liquid layer at the interface. At lock-in rotation angles, not only is the self-retraction completely suppressed (Fig. 3), but also shearing and rotating the flake with the microprobe suddenly becomes much harder. Indeed, once the interface locks in, further attempts to shear the flake generally result in a new shear interface at a different depth in the mesa (see the SM [24]).

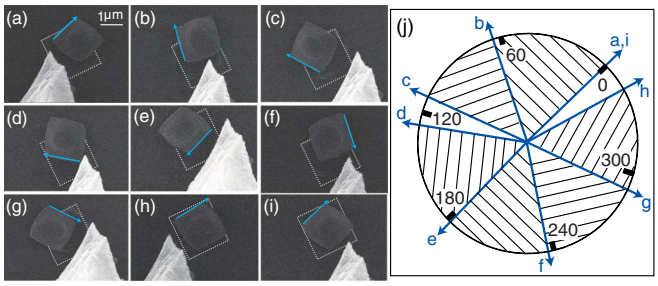

FIG. 2 (color online). *In situ* manipulation of a graphite flake in a SEM. (a)–(i) are the selected frames from Supplemental Movie 1 [24]; the orientation denoted by the arrow in each picture shows the "lock-in" orientation, where the arrow is always along the same side of the flake and the dashed squares denote the location of the graphite platform. (j) Plot of the lock-in orientations translated from (a)–(i), clearly indicating the 60° symmetry. In this plot, the 0° tick mark has been aligned with the direction of the arrow in Fig. 2(a), so that subsequent high-symmetry tick marks at 60° spacing can be compared with visual estimates of other lock-in directions. Hatched areas indicate regions between lock-in orientations where self-retraction is observed to occur reproducibly (see the SM [24]).

To compare the lock-in and self-retraction states quantitatively, we selected a tungsten microtip sufficiently pliable that it displays plastic deformation when trying to shear a flake in the lock-in orientation (Fig. 3). We observe the microtip in a quasistatic manner (see Supplemental Movies 2 and 3 [24]): attempting to shear the flake and then releasing the microtip by raising it. For the case where the flake self-retracts, the difference of the microtip apex position for loading and unloading [Figs. 3(a) and 3(b)] is beyond the resolution of optical microscopy (less than one pixel). For the case where there is lock-in, a large tip apex displacement is observed during shearing (about 30 pixels), as seen in Fig. 3(c). When unloading, the tip remains bent [Fig. 3(d)], indicating that plastic deformation has occurred while attempting to shear. The shearing resistance force in the lock-in state can be estimated from the deformation of the tip to be 0.47 ± 0.21 mN (see the SM [24]), corresponding to a strength $\tau_{\text{lock-in}} = 0.1 \pm 0.04$ GPa, which compares very well with the FFM experimental result, $\tau_s = 0.10$ GPa [7]. Furthermore, from the lack of any detectable tip bending when shearing a flake that self-retracts [Fig. 3(a)], we can deduce an experimental upper bound τ_f^{super}, which is $\tau_f^{\text{super}} < 3.3$ MPa. This is consistent with, though much less restrictive than, the upper bound deduced from the estimate of the self-retraction force. Based on the combined evidence of the experiments described above, we conclude that the self-retraction motion and the lock-in states are due to the structural superlubricity of graphite at the atomic scale.

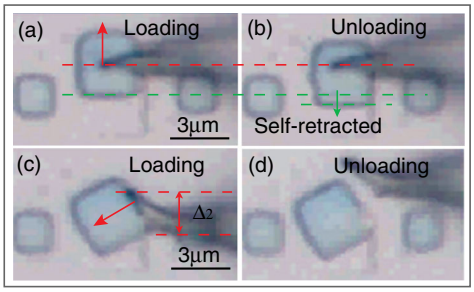

FIG. 3 (color online). (a),(b) The deformation of a microtip when moving a graphite flake that self-retracts. (c),(d) The attempt to move one that is in a lock-in state. The images are for loading (with the tip in contact with the flake during the attempt to shear) and unloading (with the tip removed from the flake surface). The images are selected from *in situ* Supplemental Movies 2 and 3 [24].

We detect no significant rotation during the self-retraction, so the flake returns to the same position and orientation as before shearing. Spontaneous rotation to a high-symmetry, high-friction state, which appears to suppress superlubricity at the nanoscale [12], does not occur here, presumably due to the much higher rotational inertia of the microscopic flakes and high self-retraction speed [25]. We also note that any dissipation effect due to the motion of misfit dislocations at the interface, as proposed in Ref. [7], appears to be negligible, presumably because the high stiffness of the graphene planes that define the interface does not allow for significant dislocation-induced atomic relaxation during motion.

Although some of our experiments are carried out in a SEM and therefore under vacuum, there is no detectable difference of the self-retraction effect for measurements made with an optical microscope in air. This is true for the friction anisotropy and the probability of self-retraction as a function of flake size. It seems that exposure of the surface to potential contamination has little effect in our system. The reason could be a self-cleaning effect of the graphite flake during the self-retraction, which has been reported previously [26].

If it is so hard to shear the flake once it is in a lock-in orientation, an obvious question arises: how are we able to shear so many of the mesas in the first place? In this connection, an important observation is that the lock-in orientations do not generally correspond to an alignment of the flake and mesa edges. We explain this as follows: when we shear mesas, they will preferentially shear at interfaces where there is already a natural incommensurate relationship between two crystallites in the HOPG. The simplest of such interfaces is a grain boundary running through the entire mesa at a certain depth below its surface. Such a grain boundary will present much lower frictional resistance to shear, enabling the superlubric motion to occur.

While we have not been able to verify this hypothesis directly, as it requires atomic-scale measurements on both sides of a microscopic interface, we have accumulated strong indirect evidence.

Using electron backscattered diffraction (EBSD) to study the free surface of the same type of HOPG used to create the mesas, we can measure the lateral size distribution of the grains that are rotationally misoriented relative to each other. The grain size is in the range of 3–60 μm, with the average about 13 μm (see Fig. S4 in the SM [24]). This distribution implies that the probability that a given mesa happens to be situated within a single grain should fall rapidly for mesas of linear dimension >10 μm. This is entirely consistent with our statistical observations of self-retraction probability as a function of mesa size. We also note from our EBSD measurements that the c axis of all the grains is aligned within a few degrees.

As noted above, when the flake locks in, attempts to shear it will generally result in shearing at a different depth. Repeating this procedure leads to multiple flake lock-ins, and an atomic force microscope measurement of the heights of these flakes, for the mesas in our study, is in the range of 11 to 60 nm (see Fig. S5 in the SM [24]). This result is consistent with the recent observation through combining focused-ion-beam/SEM and high-resolution transmission electron microscopy that, along the c-axis direction, HOPG possesses a polycrystalline structure with a grain thickness of about 5–30 nm [27]. Combining this observation with our experimental results, we believe that the stone wall polycrystalline structure depicted in Figs. 4(e) and 4(f) is a good representation for HOPG, where each brick represents a single grain consisting of nearly perfect crystalline graphite. If one or more twist boundaries traverse the mesa [Fig. 4(e)], then shearing will occur preferentially at one of these. If no twist boundary traverses the entire mesa, then shearing may still preferentially occur for twist boundaries that trasverse only part of the mesa. In this case, the result will be an uneven surface with large steps due to the grain structure [Fig. 4(f)]. The probability of the latter scenario should increase with mesa lateral dimension, as we observe.

To further test this model, we carried out scanning tunneling microscope (STM) studies on the surfaces of graphite mesas after removing a flake that showed reproducible self-retraction. A typical result is shown in Fig. 4(c), in which the height profile varies within 0.5 nm over 1.5 μm. This indicates that the interface is close to being atomically smooth. We also made STM scans for the exposed surfaces of mesas where graphite flakes did not exhibit self-retraction [Fig. 4(d)]. The height profile exhibits abrupt steplike defects several nanometers in height, which is consistent with the model that shearing has occurred at an interface that is not entirely within a single graphite grain. The number density of such surface defects is found to be in the range 0.44–2.5 per square micron in five samples.

Further evidence for this model comes from optical microscope observations where we see abrupt variations of the color of flakes sheared from the mesas for the case

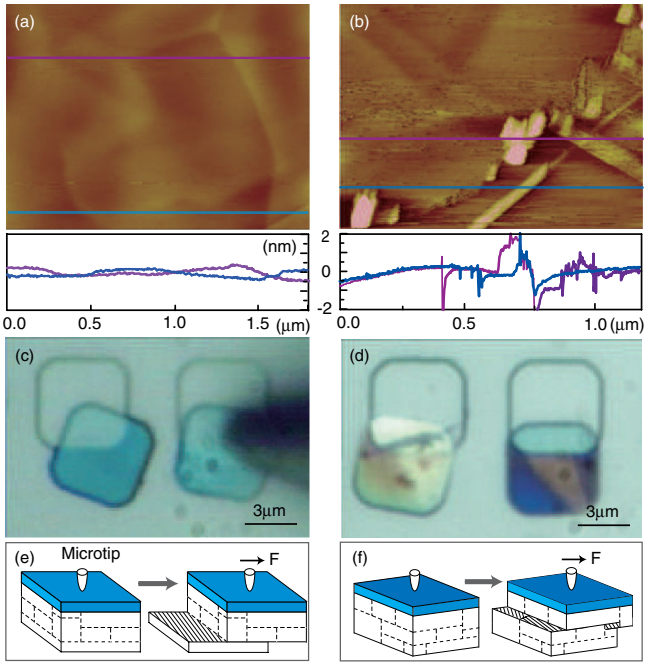

FIG. 4 (color online). (a) STM scan of the typical exposed surface of a graphite mesa that exhibits self-retraction, which indicates nearly atomic-scale smoothness, and (b) the same for a mesa that does not exhibit self-retraction, showing the appearance of significant interfacial defects. (c) shows no color variation in optical microscope observations of partially sheared flakes that exhibit self-retraction. The image is obtained by deliberately locking in the flake. (d) Abrupt color variations for flakes that do not self-retract, indicating large steps at the interface. (e),(f) are schematic representations of the proposed graphite microstructure for mesas that exhibit self-retraction [in (e), where the grain boundary traverses the entire mesa] and those that do not [in (f), shearing occurs at the boundary between multiple grains, resulting in large interface steps and defects].

where no self-retraction occurs [Fig. 4(d)], due to optical interference resulting from local thickness variations of the graphite, while, for the mesas exhibiting self-retraction, the color of the flakes is uniform [Fig. 4(c), observed by deliberately establishing lock-in]. This is a phenomenon also reported by Chang *et al.* when cleaving HOPG samples [28]. Observing many retracted graphite flakes, we could deduce the probabilities of such thickness variations in the graphite as 0%, 17%, 18%, 75%, and 89% for mesas with edge sizes of 1.7, 3.0, 5.0, 7.0, and 10.0 μm, respectively. These observations are again fully consistent with the simple stone block model of Figs. 4(e) and 4(f) and its dependence on mesa lateral dimension.

Size is a crucial factor in superlubricity [4,7]. Dietzel *et al.* reported a size-dependent superlubricity of Sb nanoparticles sliding on a HOPG surface [13]. In comparison to our system, their size scale of the superlubricity is significantly lower. The superlubricity probability of the Sb/HOPG system drops from 50% to 20% for contact areas from 1×10^4 to 9×10^4 nm^2 and becomes zero

above 9×10^4 nm^2. Our graphite mesa system exhibits 100% superlubricity for contact areas below 1×10^6 nm^2 and a gradual probability drop from 58% to 12% for contact areas from 2.89×10^6 to 1×10^8 nm^2. The superlubricity completely disappears above a contact area of 4×10^8 nm^2. We explain the difference by noting that the Sb/HOPG system is very sensitive to surface contamination even under ultrahigh vacuum conditions [13]. Our graphite mesa, on the other hand, is almost immune to the contamination because of the self-cleaning effects [26]. It is the inherent structural defects of the two contact surfaces that suppress the superlubricity. Our graphite mesa, therefore, provides an excellent platform to study superlubricity in a size scale from nm^2 to hundreds of μm^2 and to reveal the inherent interface structural effects. It bridges the gap between the <10 nm^2 contact area of scanning probe microscopes and the $>10^4$ μm^2 contact area offered by the surface force apparatus.

In summary, we have demonstrated for the first time direct evidence for reproducible structural superlubricity on the micron scale and even under ambient conditions, using self-retraction of sheared graphite mesas as a novel way of probing this form of ultralow friction. Based on measurements of the grain structure of the graphite, we argue that shearing occurs preferentially at grain boundaries that traverse the microscopic mesas. By tuning the mesa size, it is possible to tailor superlubricity in lithographically defined graphitic micromechanical devices.

We thank Z. P. Xu, Z. H. Li, H. W. Zhu, and X. Yang for their helpful discussions. Q. S. Z. acknowledges the financial support from NSFC through Grant No. 10832005, the National Basic Research Program of China (Grant No. 2007CB936803), and the National 863 Project (Grant No. 2008AA03Z302). J. Z. Liu appreciates the support of a new staff grant and a seed grant from the engineering faculty at Monash University.

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[1] M. Urbakh and E. Meyer, Nature Mater. **9**, 8 (2010).
[2] C. G. Lee, Q. Li, W. Kalb, X.-Z. Liu, H. Berger, R. W. Carpick, and J. Hone, Science **328**, 76 (2010).
[3] B. Bhushan, J. N. Israelachvili, and U. Landman, Nature (London) **374**, 607 (1995).
[4] M. Hirano and K. Shinjo, Phys. Rev. B **41**, 11 837 (1990).
[5] M. Hirano, K. Shinjo, R. Kaneko, and Y. Murata, Phys. Rev. Lett. **67**, 2642 (1991).
[6] M. Hirano, K. Shinjo, R. Kaneko, and Y. Murata, Phys. Rev. Lett. **78**, 1448 (1997).
[7] M. Dienwiebel, G. S. Verhoeven, N. Pradeep, J. W. M. Frenken, J. A. Heimberg, and H. W. Zandbergen, Phys. Rev. Lett. **92**, 126101 (2004); G. S. Verhoeven, M. Dienwiebel, and J. W. M. Frenken, Phys. Rev. B **70**, 165418 (2004).
[8] J. M. Martin, C. Donnet, Th. Le Mogne, and Th. Epicier, Phys. Rev. B **48**, 10 583 (1993).
[9] A. Socoliuc, R. Bennewitz, E. Gnecco, and E. Meyer, Phys. Rev. Lett. **92**, 134301 (2004).
[10] M. Dienwiebel, N. Pradeep, G. S. Verhoeven, H. W. Zandbergen, and J. W. M. Frenken, Surf. Sci. **576**, 197 (2005).
[11] E. Gnecco, S. Maier, and E. Meyer, J. Phys. Condens. Matter **20**, 354004 (2008).
[12] A. E. Filippov, M. Dienwiebel, J. W. M. Frenken, J. Klafter, and M. Urbakh, Phys. Rev. Lett. **100**, 046102 (2008).
[13] D. Dietzel, C. Ritter, T. Mönninghoff, H. Fuchs, A. Schirmeisen, and U. D. Schwarz, Phys. Rev. Lett. **101**, 125505 (2008).
[14] *Superlubricity*, edited by A. Erdemir and J.-M. Martin (Elsevier, Amsterdam, 2007).
[15] K. Miura, D. Tsuda, and N. Sasaki, e-J. Surf. Sci. Nanotechnol. **3**, 21 (2005).
[16] Q.-S. Zheng, B. Jiang, S. Liu, Y. Weng, L. Lu, Q. Xue, J. Zhu, Q. Jiang, S. Wang, and L. Peng, Phys. Rev. Lett. **100**, 067205 (2008).
[17] X. K. Lu, M. Yu, H. Huang, and R. S. Ruoff, Nanotechnology **10**, 269 (1999).
[18] M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, Science **287**, 637 (2000).
[19] M. F. Yu, Yu. Boris, and R. S. Ruoff, J. Phys. Chem. B **104**, 8764 (2000).
[20] J. Cumings and A. Zettl, Science **289**, 602 (2000).
[21] Q.-S. Zheng and Q. Jiang, Phys. Rev. Lett. **88**, 045503 (2002); Q.-S. Zheng, J. Z. Liu, and Q. Jiang, Phys. Rev. B **65**, 245409 (2002).
[22] Z. Liu, J. Z. Liu, Y. Cheng, Z. Li, L. Wang, and Q.-S. Zheng, arXiv:1104.1469v1 [Phys. Rev. B (to be published)].
[23] F. Bowden and D. Tabor, *The Friction and Lubrication of Solids* (Oxford University, Oxford, 1950).
[24] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.108.205503 for *in situ* movies of manipulating self-retractable graphite flakes in SEM and an optical microscope, a statistical analysis on the self-retraction motion, a mechanical model analyzing the shear strength in A/B stacking, the EBSD experimental measurements of HOPG, and the multishearing of graphite flakes.
[25] A. S. de Wijn, C. Fusco, and A. Fasolino, Phys. Rev. E **81**, 046105 (2010).
[26] Z. Liu, P. Bøggild, J.-R. Yang, Y. Cheng, F. Grey, Y.-L. Liu, L. Wang, and Q.-S. Zheng, Nanotechnology **22**, 265706 (2011).
[27] S. Y. Park, H. C. Floresca, Y. J. Suh, and M. J. Kim, Carbon **48**, 797 (2010).
[28] H. Chang and A. J. Bard, Langmuir **7**, 1143 (1991).