

## Self-Retracting Motion of Graphite Microflakes

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We report the observation of a novel phenomenon, the self-retracting motion of graphite, in which tiny flakes of graphite, after being displaced to various suspended positions from islands of highly orientated pyrolytic graphite, retract back onto the islands under no external influences. Reports of this phenomenon have not been found in the literature for single crystals of any kind. Models that include the van der Waals force, electrostatic force, and shear strengths were considered to explain the observed phenomenon. These findings may conduce to create nanoelectromechanical systems with a wide range of mechanical frequency from megahertz to gigahertz.

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Graphite is one of the most useful materials because of its many extreme mechanical, electrical, and thermal properties as well as biocompatibility. For example, due to the superlubricity [1,2] between graphite layers and the extreme high elastic moduli and strengths within the layers, graphite has widely been used as durable solid lubricants. New surprising properties of graphite have been discovered at times, such as the existence of a graphite monolayer in the free state [3] and extreme anisotropy owned by graphite compared with all other hexagonal crystalline materials [4]. The former provides an ample scope for fundamental research and new technologies [5] and has already prompted intensive studies, such as designable electrical properties [6–8] and the quantum Hall effect [9]. Unlike the carbon nanotubes or other low-dimensional nanostructured materials, graphene nanoribbons with intricate submicrometer structures can now be fabricated [6,10], leading to the use of the graphite sheet structure to fabricate an electromechanical resonator [11] or electronic junction [12].

The recent experiments on controlled sliding and extraction releasing of nested shells in individual multiwalled carbon nanotubes (MWNTs) [13,14] revealed that the MWNTs have similar superlubricity as graphite, with the interwall shear strength against sliding ranging from 0.08 to 0.3 MPa. For comparison, the interlayer shear strength values of high quality crystalline graphite range from 0.25 to 0.75 MPa varying with shear directions, and those

between rotated graphite layers are 1 order lower in magnitude [2]. More interestingly, some extracted inner shells were found to self-retract back into the outer shells [14] and were well explained to be derived by van der Waals interaction [14,15]. Inspired by these observations, MWNT-based oscillators as the first sample nanoelectromechanical system with frequencies in the gigahertz range were proposed [15] and then intensively studied [16].

When people drew or wrote using pencils, they produced countless tiny pieces of graphite, each consisting of many graphene sheets [see Fig. 1(a)]. Considering that the interlayer interaction of graphite is of the same nature as the interwall interaction of MWNTs, we have wondered whether or not one can generate a similar self-retracting motion for graphite, in view of the fact that its interlayer slipping phenomenon has been known for a long time. We have thus explored this issue, and with this Letter, we have documented our detailed observations and analysis.

The experiments were carried out on square graphite-SiO<sub>2</sub> islands of the height of about 200 nm and various side lengths (sizes),  $L$ , ranging from 0.5 to 5  $\mu\text{m}$  [see Figs. 1(b) and 1(c)]. The technique we used to prepare such islands is similar to that reported in [17], as detailed below. As illustrated in Fig. 1(b), we first deposited a SiO<sub>2</sub> film about 100 nm in thickness by controlling the deposition time onto a freshly cleaved surface ( $5 \times 5$  mm) of a HOPG sample, using plasma enhanced chemical vapor deposition. Second, we patterned it into squares with nega-

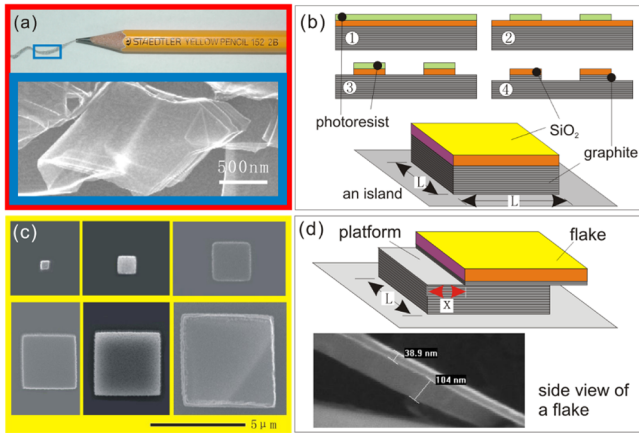


FIG. 1 (color online). Flakes: (a) countless tiny graphite pieces produced as drawing with a 2B pencil; (b) illustrative steps for carving square graphite-SiO<sub>2</sub> islands from a highly oriented pyrolytic graphite (HOPG) coated with a SiO<sub>2</sub> film; (c) top views of some samples of square islands; (d) an illustration of a slipped flake, its graphite platform, and a scanning electron microscope (SEM) side view of an overturned flake showing it to consist of a SiO<sub>2</sub> film of thickness 104 nm and graphite lamina of thickness 38.8 nm.

tive photoresist (*PmmA495*) by spin coating onto the surface of the SiO<sub>2</sub> film and by electron beam lithography. Third, the portion of the SiO<sub>2</sub> film, unprotected by the photoresist, was etched away by reactive ion etching. Fourth, the remaining portion of the SiO<sub>2</sub> film was then used as the masking surface in a follow-up oxygen plasma etching to remove the photoresist. This led to the final graphite-SiO<sub>2</sub> square islands, as illustrated in Fig. 1(b).

The experiment on each tested graphite-SiO<sub>2</sub> island was carried out by controlling the probe of a micromanipulator *mm3A* (Kleindiek) set in a SEM to laterally push an upper edge or horizontally rub on the top surface of the island [see Figs. 2(a) and 2(b)]. The probes were selected to have similar tip sizes as the tested islands. Their lateral motions, up to 5 nm in accuracy, were manually controlled by rotating a knob of the micromanipulator. The moving probe and flakes were monitored in both image and digital controllers. With this method we successfully slipped out a flake from each of the tested dozens of islands of 1 or 2  $\mu\text{m}$  side length to various prescribed suspended positions. From an overturned 2  $\mu\text{m}$  flake [see Fig. 1(d)], we found that it consists of a 104-nm-thick SiO<sub>2</sub> film and a 38.8-nm-thick graphite lamina. Thus, the underlying square platform is purely graphitic and both contact surfaces are graphite basal planes. Furthermore, we found that each suspended flake under test can automatically and fully retract back onto the graphite platform top immediately after the applied force is released by removing the probe away from the flake. The observation that the retracting motion occurred even though the probe was removed away in the direction opposing the retraction motion direction

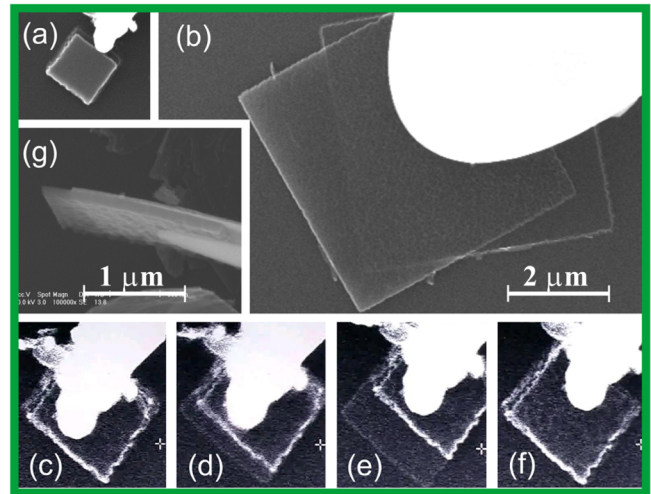


FIG. 2 (color online). The slip and self-retraction of flakes: (a) slip without rotation, (b) slip with rotation, (c)–(f) selected frames of a video recording of the *in situ* backward slipping (c)–(e) and retracting (f) of a 1  $\mu\text{m}$  island (see the EPAPS movie [18]); (g) the wrapped microflake slipped from a 5  $\mu\text{m}$  island and did not self-retract the multiflake slip. Scale bar for (a),(b) is 2  $\mu\text{m}$ , and that for (c)–(g) is 1  $\mu\text{m}$ .

[see Figs. 2(c)–2(f) and the EPAPS movie [18]] excludes the qualm that the retracting motion would be caused by the adhesion or electrostatic force between the flakes and the removing probe, and this thus validates the term “self-retracting motion.”

The slip and self-retraction processes were easily repeated again and again, and many of them were accompanied with rotations [see Fig. 2(b)], particularly when the slip forces were eccentrically applied. In addition, the different deformations of the probe, measured by the observed flake displacements and recorded knob rotations, reveal that the resistance against initiating the slip motion is significantly larger than the resistance during motion. After having either rotational or repeatedly translational slips, the sliding resistance was found to be even smaller. However, in these cases that we released the applied force after we had taken a pause of 15–20 s to record a high resolution SEM image of a flake in its suspended position, we found that the flake stayed at the suspended position and we observed no self-retraction. Interestingly, self-retraction of this flake was again observed after slipping it further outward and then immediately releasing it, while the self-retraction motion, however, returned it only to the previous stop position. For a possible explanation, we have noted previous reports [19] that amorphous carbon layers of several nanometers in thickness were formed within 20 s on surfaces exposed in electron beams of the SEM. We have also found that repeating the slip-retraction process may generate several graphite flakes under the top graphite-SiO<sub>2</sub> flake, and correspondingly, the self-retracting motion becomes multibody motion.

It was observed that slipped flakes are not always self-retracting, even if released immediately after slipping, depending upon the island size and whether or not a flake was rotated when it was slipped. For islands of  $3.5 \mu\text{m}$  size length, this self-retracting motion was observed for most of the slipped and rotated flakes, but only for some of the flakes that were slipped without rotation. For the  $5 \mu\text{m}$  islands, the self-retracting motion was only occasionally observed for slipped and rotated flakes, but was never observed for the nonrotated ones. This indicates that the probability of the self-retraction decreases substantially with the increasing side length of the flakes. We have tested 15 slipped flakes for each island size, and our observations indicate that probabilities were 100% for 1 or  $2 \mu\text{m}$  islands, and 87%, 33%, and 13%, respectively, for 3.0, 3.5, and  $5.0 \mu\text{m}$  islands. These observations suggest the existence of rotation-dependent critical or maximum sizes under the described slip operation, approximately  $3\text{--}5 \mu\text{m}$ , to permit the self-retracting motion. This helps to explain the fact that the graphite self-retracting motion was not previously observed because samples of natural graphite are typically larger than the critical sizes. In addition, our attempts of slipping out flakes from  $0.5 \mu\text{m}$  size islands, however, had always led to overthrow the islands. Furthermore, we found that the stiff  $\text{SiO}_2$  coats play a key role for realizing the self-retracting motion. After having removed the  $\text{SiO}_2$  coats from some islands of various side lengths, we failed to slide out any flakes without rolling or buckling the graphite monolayers on the coat-removed islands.

To further explain these observations, we consider a simple self-retracting motion of a flake that was slipped out for a distance  $x$  from an island of side length  $L$  along a side direction without rotation [see Fig. 1(d)]. The internal forces between the flake and the platform that can be associated with the self-retracting motion consist of, to the first order, the van der Waals force, static and dynamic frictional forces [14], and possible electrostatic force. The van der Waals interaction energy between the flake and the graphite platform can be estimated [20] as  $U(x) = -C_{\text{vdW}}L(L-x)$  with  $C_{\text{vdW}} \approx 0.41 \text{ J}$  by using a typical 6–12 Lennard-Jones potential. Lowering the van der Waals energy by increasing the flake-platform contact area tends to retract the flake. The van der Waals force is given by  $F(x) = -dU(x)/dx$ , and, therefore, the retraction force is constantly  $F_{\text{vdW}} = -F(x) = C_{\text{vdW}}L$  for any  $x < L$ . If electrostatic force can be excluded, then for the self-retracting motion to take place the retraction force  $F_{\text{vdW}}$  must exceed the resistance force,  $F_r$ , that is equal to  $L(L-x)\tau_s$  for initiating the retracting motion or  $L(L-x)\tau_d$  during the retracting motion, where  $\tau_s$  and  $\tau_d$  denote the static and dynamic graphite shear strengths between non-rotated graphite layers. The values of  $\tau_s$  were measured to arrange from 0.27 to 0.75 MPa (mean value 0.48 MPa [21]) depending on the sliding direction, and the values of  $\tau_d$

were found to be 1 order in magnitude smaller than those of  $\tau_s$  [1,2]. Using the initiation condition of the self-retracting motion  $F_{\text{vdW}} > F_r = L(L-x_0)\tau_s$  from a typical initial position  $x_0 = L/2$ , we obtain the estimate that the critical side length  $L_{\text{cr}}$  ranges from 1 to  $3 \mu\text{m}$  for nonrotated flakes. This agrees well with our observations. We further examine the self-retracting condition for a rotated flake. We should expect that the retraction driving force for a rotated microflake is a little bit smaller than but in the same order as that for a nonrotated one. However, the static graphite shear strengths  $\tau_s^*$  between rotated graphite layers are 1 order smaller than  $\tau_s$ . These imply that the self-retracting motion may occur for rotated flakes with side lengths of several to tens of micrometers.

To understand why in our experiments the self-retracting motion was observed only for a few  $5 \mu\text{m}$  flakes, we lifted a  $5 \mu\text{m}$  non-self-retracted flake and noted its warped shape [see Fig. 2(g)]. This indicates that the flake had experienced a deformation exceeding the elastic range. Because the retraction force  $F_{\text{vdW}}$  results from the van der Waals interaction, it reduces rapidly to zero as the separation spacing between the flake and the platform increases from the optimized value  $s_0 = 0.335 \text{ nm}$ . For example, using the 6–12 Lennard-Jones potential [20] we estimated  $F_{\text{vdW}}$  at  $s = 2 \text{ nm}$  to be less than 1% of the value of  $F_{\text{vdW}}$  at  $s = s_0$ . Consequently, the retraction driving force  $F_{\text{vdW}}$  of a warped flake would be much smaller than that of a flat flake. Thus, it is likely that  $F_{\text{vdW}}$  of the observed warped flakes in our experiment were too small to drive the retracting motion. To understand why the flake was warped, we note that to slip out a flake, the applied force through the micromanipulator probe must exceed the sum of the static interlayer shear strength force,  $F_r = L^2\tau_s$ , and the edge interlayer dangling bond interaction,  $F_{\text{db}} = 4L\tau_{\text{db}}$ , where  $\tau_{\text{db}}$  characterizes the edge interlayer dangling bond interaction strength. Because the resistance force,  $L\tau_s + 4L\tau_{\text{db}}$ , against the initiating slip of flakes increases with the increasing flake size  $L$ , and because the thickness of the  $\text{SiO}_2$  coats the main bodies against warping deformation, and their elastic limits are fixed, the permanent deformations, like warping, of flakes slipped in our experiments should be size dependent and occurred only for larger flakes. Consequently, slipped flakes with a size larger than  $5 \mu\text{m}$  would be more severely distorted from the flat configuration, and they thus are much more unlikely to self-retracting. This explanation does not contradict the prediction of our above analysis that larger flakes, up to several tens of micrometers in size, may still experience self-retracting motion if they would remain flat and were rotated.

The above-reported experiment was carried out inside a SEM where strong electric effects can never be ruled out, and charge should be able to build up on the  $\text{SiO}_2$  surface. To exclude that the behavior would be mainly due to strong electrostatic effects, we performed an experiment under an



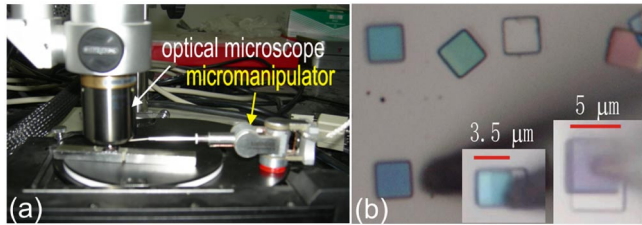


FIG. 3 (color online). Self-retracting motion observed under an optical microscope (HiRox KH-3000). (a) Manipulation and observation under the optical microscope in a room circumstance. (b) Unslipped and slipped flakes (insets captured from two retracting motion movies).

optical microscope (HiRox KH-3000) in a normal room circumstance [Fig. 3(a)]. We connected both the probe tip and the island in the experiment to the general ground and used the probe tip to eliminate a possible static charge on the SiO<sub>2</sub> surface prior to the sliding and releasing operations. We observed the similar self-retraction behavior [see Fig. 3(b) and the EPAPS movie [18]] as that reported above inside a SEM. Furthermore, it was recently observed [22] that neutral patches of the order of microns in HOPG can still have electric potential fluctuations with differences up to 0.35 V. The generated electrostatic force between the flake and the platform may either increase or reduce the retraction force from the constant value  $F_{\text{vdW}}$ , depending upon the potential distribution and slipped position. However, our primary analysis shows that this electrostatic perturbation to the retraction force is likely 2 orders lower in magnitude than  $F_{\text{vdW}}$  if the potential difference is bounded to 0.35 V. This analysis is based on an assumption that the dielectric constant between the regular graphite interlayer spacing 0.335 nm would be the one for vacuum, while there may be a factor of 10 (or more) increase in the dielectric constant that would lead to the same factor increase in the estimated electrostatic force. Therefore, further study on electrostatic force effects will be a key issue not only for a deeper understanding of the reported self-retraction behavior, but also for exploring a new class of promising nanoelectromechanical systems based on the flake-platform system.

What we have presented above is the first observation, to the best of our knowledge, of the self-retracting motion of graphite flakes slipped from graphite platforms. We expect that the self-retracting motion of the same nature occurs in other lamellar solids that are of superlow interlamellar shear resistance strengths, such as molybdenum disulphide, biotite, and phlogopite. Furthermore, we expect to observe the self-retraction motion if one places a carbon nanotube on a graphite platform and pushes it to a suspended position. The findings reported in this Letter may conduce to create nanoelectromechanical systems with a wide range of mechanical operating frequency from megahertz to gigahertz. In fact, with the same physical principle

for predicting the ultrafast MWNT oscillator [15], the self-retracting motion of graphite flakes could be used to fabricate oscillators with frequencies in a wider range than that of MWNT oscillators.

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