Superlubricity of graphene nanoribbons on gold surfaces

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The state of vanishing friction known as superlubricity has important applications for energy saving and increasing the lifetime of devices. Superlubricity, as detected with atomic force microscopy, appears when sliding large graphite flakes or gold nanoclusters across surfaces, for example. However, the origin of the behavior is poorly understood because of the lack of a controllable nanocontact. We demonstrated the superlubricity of graphene nanoribbons sliding on gold with a joint experimental and computational approach. The atomically well-defined contact allows us to trace the origin of superlubricity, unraveling the role played by ribbon size and elasticity, as well as by surface reconstruction. Our results pave the way to the scale-up of superlubricity and thus to the realization of frictionless coatings.

Graphene offers distinctive properties as a solid lubricant (I) and has the potential to be used as an ultrathin coating material on surfaces, almost suppressing energy consumption in mechanical components. The interpretation of such superlubric behavior is based on the premise that (2–5) (i) the high lateral stiffness of graphene makes a commensurable contact with most solid surfaces nearly impossible, and (ii) combined with the weak interaction with most materials, incommensurability leads to a state of ultralow friction when graphene slides over a different material. To substantiate this hypothesis and establish a connection with the tribological properties observed on macro- and mesoscales, it is highly desirable to measure the mechanical response of a graphene flake down to the nanometer level. In such measurements, one has to ensure that both of the contacting surfaces are atomically well defined, that their common interface is free from contaminants, and that the ultralow forces accompanying the sliding motion can be distinguished from the background noise. Whereas clean atomically flat surfaces as substrates can reliably be obtained in ultrahigh vacuum (UHV), atomically defined graphene systems as sliding objects are rarely prepared. Carbon nanotubes have exceptional superlubric properties up to a length scale

Fig. 1. Static friction force measurement. (A) STM topographies of GNRs on Au(111) before and after a tip-induced lateral manipulation (the green arrow indicates the sliding direction). (B) 2D Δf map along the longitudinal axis of the manipulated GNR. (C) Distance dependence of Δf before, during, and after the GNR displacement. (D) Calculated lateral force. The cross symbol corresponding to the red arrow in (B) shows the position at which the GNR starts moving and the corresponding value of the static friction force $F_{\text{stat}}$. (E) The absolute value of $F_{\text{stat}}$ as a function of the GNR length (black) and $F_{\text{stat}}$/per unit length (red). Dots correspond to single measurements, whereas bars connect the largest and the smallest values measured while manipulating the same ribbon on different surface regions. Measurement parameters: tunneling current $I = 2$ pA, bias voltage $V = -200$ mV (A); oscillation amplitude $A = 34$ pm ([B] to [D]).
of a few centimeters (6), but their curvature makes them difficult to manipulate in a controlled way. Nevertheless, the problem can be overcome by using graphene nanoribbons (GNRs), which recently have been synthesized on a metal substrate by means of an on-surface chemical reaction (7). Their structure is well defined by the precursor molecule, as confirmed by high-resolution scanning tunneling microscopy (STM) and atomic force microscopy (AFM). For this reason, GNRs are an appropriate candidate for our goal. Apart from that, GNRs are also very promising in a series of applications (e.g., nanoelectromechanical systems (8), nanofillers (9), transistors (10), and other electronic and spintronic devices (11)) for which assessing their mechanical stability is pivotal.

We investigated the frictional, adhesive, and elastic properties of GNRs by means of lateral manipulation on an Au(111) substrate, using dynamic AFM in UHV at a low temperature (4.8 K). The ends of selected GNRs were anchored to the probing tip and dragged back and forth in a controlled way while the friction force was recorded. An accompanying computational experiment allowed us to relate the origin of the measured superlubricity to the molecular dynamics occurring at the interface.

Our measurements originate from the unintentional manipulation of GNRs aligned along the [-1,0,1] direction of the Au(111) substrate, when the GNRs were imaged by STM using a gold tip. The GNRs were always displaced along their longitudinal axis, even with a relatively large separation, indicating high diffusivity (figs. S1 to S4).

To measure the static friction force ($F_{\text{stat}}$), we switched to AFM, using the same tip. After imaging a sample area covered by GNRs (Fig. 1A), we acquired a two-dimensional (2D) frequency shift map while the tip was scanned laterally along a GNR ($x$ direction) at different constant $z$ distances (Fig. 1B and fig. S5). Following the method of Ternes et al. (12), we reduced the tip-GNR distance stepwise during scanning until we observed an abrupt decrease in the frequency shift ($\Delta f$) at the distance defined as $z = 0$ (Fig. 1C). We found that the GNR was displaced by a distance $d = 2.2$ nm (Fig. 1A). We also observed that the $\Delta f(z)$ profile was repeated after the same distance. Langewisch et al. reported a similar observation in their manipulation experiments on perylenetetracarboxylic diimide molecules (13). We found that $d$ varied with both the GNR length and the adsorption site. Furthermore, jumps with smaller $d$ values were rarely observed, and the GNRs were never dragged continuously, meaning that the junction formed between the tip and the GNRs is weak. To quantify $F_{\text{stat}}$, we first estimated the energy landscape experienced by the tip by integrating two times the $\Delta f(z)$ sections extracted from Fig. 1B. Then we differentiated the 2D potential map along the $x$ direction and multiplied the result by the factor $-2k_f/\pi = 0.15 \text{ N m}^{-1} \text{ Hz}^{-1}$, where $k_f = 1800 \text{ N m}^{-1}$ is the spring constant, and $f = 24.7 \text{ kHz}$ is the resonance frequency of the free tuning fork. The manipulation occurred when $F_{\text{stat}} = -105 \text{ pN}$ (Fig. 1D). $F_{\text{stat}}$ is exceptionally low, considering that the linear size of the GNR is well above that of the single atoms and conventional molecules that are typically manipulated by AFM (12, 14, 15). This result is a strong confirmation of the superlubric properties of graphene on the nanoscale, as observed in previous friction measurements taken on graphene flakes of undefined size (16-18). Another signature of superlubricity is the decrease of the friction force per unit of contact area with increasing size of the contact (19-22). To look for this, in our quasi-1D system, we repeated the measurements on GNRs of different lengths (Fig. 1E).

In spite of the spread in the measured data (due to the surface reconstruction, discussed below), the force per unit length was found to decrease with increasing GNR length.

We estimated the diffusion barrier ($\Delta E$) for the GNR by assuming a simple sinusoidal interaction as $\Delta E = F_{\text{stat}}a/\pi \approx 40 \text{ meV}$, where $a = 0.41 \text{ nm}$ is the lattice constant of the Au(111) substrate (25). This low value means that a single isolated GNR would diffuse spontaneously at room temperature, making measurements challenging. We also observed a rotation of short GNRs (2 nm), although we always scanned the tip exactly along the GNR axis (fig. S6). This behavior is predicted theoretically for graphene flakes dragged on graphite (22). We even observed a vertical motion of the shortest GNRs (1 nm) before the start of lateral manipulation (fig. S7).

We could not perform reliable static friction force measurements on GNRs longer than 22 nm, because other GNRs were often found nearby, and the measured forces were considerably affected by the interaction with those neighbors. Nevertheless, superlubricity allowed us to manipulate GNRs up to 55 nm long (figs. S8 and S9).

Although our measurements allow a precise estimation of the static friction force, they do not provide any details on the complex dynamics of the sliding motion of the GNRs. To gain more insight, we applied the procedure that some of us previously introduced for polymer chains (23) and succeeded in attaching a short edge of a GNR to an Au-coated tip. We then oscillated the GNRs along the [-1,0,1] direction of the Au(111) surface with the tip kept at a constant distance ($z$) from the substrate. We repeated the measurements several times at increasing values of $z$ (Fig. 2A). The corresponding variations in $\Delta f$ are shown in Fig. 2C to F, for increasing values of $z$. We found...

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**Fig. 2. Frequency shift versus pulling height.** (A) Schematic drawing of the lateral manipulation procedure. (B) STM topographies before and after a GNR has been displaced on the Au(111) surface in the direction of the yellow arrows. The length of the GNR is 6.28 nm, corresponding to seven connected monomers. (C to F) Frequency shifts accompanying the lateral motion at different heights ($z = 2, 3, 4,$ and 5 nm). Oscillation amplitude $A = 38 \text{ pm}$. 

that the frequency shift oscillated with a periodicity of 0.28 nm, except when the GNR was driven backward with a tip–surface distance of \( z = 5 \) nm. The amplitude of the \( \Delta f \) oscillations was not constant along \( x \) but modulated on distances of a few nanometers, varying by a factor of 2. We observed curves with roughly half-periodicity at a small scanning distance of \( z = 1 \) to 2 nm (figs. S10 and S11). We also imaged the sample at the end of the process to ensure that we manipulated only the target ribbon (Fig. 2B and fig. S12).

Figure 3 and fig. S13 show the variations of the normal force \( F_z \) and lateral force \( F_x \), calculated by molecular dynamics (MD) simulations, as the tip drives the GNR parallel to the unreconstructed Au(111) surface at a low separation (\( z = 2 \) nm). Two characteristic lengths of 0.06 and 0.11 nm correspond to the lateral shift between three stable configurations (Fig. 3C). We estimated \( \Delta f \) as recorded in the AFM measurements by multiplying the force derivative \( [F_x(z, z+\Delta z) - F_x(z, z)]/\Delta z \) by the conversion factor 0.15 N m\(^{-1}\) (\( \Delta z = 0.05 \) nm). The obtained profile (Fig. 3B) maintains the same periodicities of the manipulation curves, allowing comparison between simulations and experiments, although the relative heights of the peaks are different.

The regular profile (Fig. 3B) is considerably modified by the herringbone reconstruction, which deforms the top Au(111) layer and makes it slightly wavy (0.02-nm corrugation). The commensurability degree between the GNR and the substrate is modulated correspondingly, and the same modulation appears in the friction (or frequency shift) profiles. We studied via our simulations the effect of the reconstruction starting at three different locations on the surface (Fig. 3, D to G). The friction force is reduced if the whole GNR lies on the face-centered cubic (FCC) or hexagonal close-packed (HCP) regions (red arrows), is still small when the GNR crosses the boundary between the FCC and HCP regions (green arrow), but increases and reaches a maximum value when the free edge of the GNR or the point of detachment from the substrate sits over the boundary between the FCC and HCP regions (blue arrows). The GNR short edge binds more strongly to the substrate than to the inner atoms, and this effect is more pronounced in the boundary regions between HCP and FCC, where the substrate structure becomes more commensurate with that of the GNR. We established further support for this behavior by means of additional measurements taken on different GNRs (fig. S10); it is also supported by theoretical studies on the pinning role of the nanostucture edges (24). The role of the herringbone reconstruction is confirmed by a

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**Fig. 3. Simulated sliding behavior.** (A) Lateral force \( F_x(x, z) \) (blue curve) and normal force \( F_z(x, z) \) (orange curve) while pulling the 6.28-nm GNR along its longitudinal axis at a distance \( z = 2 \) nm from an unreconstructed Au(111) surface. The force \( F_z \) has been also calculated at \( z = 2.05 \) nm (green curve), which allows us to estimate the frequency shift variation \( \Delta f(x) \) shown in (B). (C) Sketch of a generic row of C atoms in the GNR (black), showing that most of the time, the atoms sit in three nonequivalent configurations marked as 1, 2, and 3 (also marked in other panels); these configurations give rise to a periodicity of \(-0.06 \) nm for short jumps from 1 to 2 or \(-0.11 \) nm for long jumps from 2 to 3 or 3 to 1 (Au atoms are shown in orange). (D) Tip trajectories on reconstructed Au(111) for the scan of panels and GNR configurations corresponding to minimum and maximum friction (the simulation cell size is 25.7 \( \times \) 7.0 nm). Dashed lines represent the boundaries between the HCP and FCC regions, and rectangles represent the attached portion of the GNR during the scan (with red, green, and blue colors corresponding to increasing lateral force). In the background, dots indicate C atoms and surface, middle, and inner layers. (E to G) Frequency shift \( \Delta f(x) \) along the scan lines in (D). The corresponding lateral force profiles are shown in fig. S13.
similar experiment that we attempted on an unreconstructed Ag(111) surface. In this case, the GNRs merged and formed a moiré pattern with the substrate (fig. S14). Manipulation with force values similar to those used on Au(111) was not possible in this case.

Configuration 2 of the GNR (Fig. 3C) becomes unstable as the transitions from 1 to 2 and from 2 to 3 are suppressed. This leads to the half-periodicity that we sometimes observed while scanning at very close separations. Just before a “slip” from 1 to 3 or 3 to 1 occurs, the GNR becomes almost insensitive to the substrate, except for its short edge, which is still attached to the substrate (fig. S15). Because a C atom at this edge lies in a potential well \( U_0 \) a few milli-electron volts deep, and it is essentially driven by the spring \( k = 1.5 \text{ N m}^{-1} \) that connects the GNR to the tip apex [C-C bonds have an estimated stiffness of a few hundred newtons per meter (25)]. We can apply a well-known result of the Frandt-Tomlinson model for atom-scale friction and estimate the characteristic parameter \( \eta = 4k^2 \sqrt{U_0/(k \alpha^2)} \) (26). The resulting value of \( \eta \) is well below 1 and indicates a continuous transition between the two equilibrium states (this is valid strictly at the particular instant that we have considered). When the GNR is pinned in configuration 1 or 3 and is pulled by the spring at the same time, all C atoms in contact with the substrate oppose a certain resistance, but the overall value of the friction force remains very small (a few hundred piconewtons). Thus, our MD simulations are fully consistent with the commonly accepted interpretation of the superlubricity of graphene. Because of its exceptional lateral stiffness, this material is not prone to stretch and adapt to the substrate lattice while sliding. Combined with the weak interaction between graphene and the substrate, the resulting incommensurability leads to the almost frictionless sliding of the GNR.

We plotted \( \Delta f/(z) \) curves at increasing separations \( z \) from the surface and also reversed the direction of motion (Fig. 4). Configuration 1 becomes unstable when \( z > 2 \text{ nm} \), and only the 3-to-3 transitions remain (corresponding to the more frequently measured periodicity of 0.28 nm). Lastly, we noticed that the forward and backward scan traces can be either in phase or in antiphase. MD simulations allow us to attribute this effect to the different bending of the suspended portion of the GNR in the two directions (Fig. 4). In the substrate regions with a large friction force, the bending of this portion can be much larger when scanning backward, thus leading to a delay in the slip events (fig. S16). If \( z = 5 \text{ nm} \) (i.e., when the GNR is close to complete detachment), the agreement between the model and experimental results becomes weak; this is presumably due to the fact that the H atoms passivating the GNR edges, which are neglected in the MD simulations, start to play an important role at this point.

The pinning and releasing processes that occur in a sliding contact, as described here, are pivotal in the development of friction between two solid surfaces in reciprocal sliding (27). The GNR-Au(111) contact is almost superlubric, with static and kinetic friction force values in the range of 100 pN. The detailed dynamics of the sliding motion are nevertheless influenced by local surface properties, such as the variable degree of commensurability caused by the surface reconstruction. These details are clearly observable when the tip-surface separation \( z \) is small but tend to disappear as \( z \) increases and the bending (elastic) properties of the suspended piece of GNR become important. Our findings will aid in understanding and improving AFM-based nanomanipulation techniques and will motivate the design of novel nano-functionalized interfaces for friction control.

Fig. 4. Simulated frequency shifts at different pulling heights. (A to D) Frequency shifts for forward and backward scans at \( z = 2, 3, 4, \) and 5 nm. Note that the half-periodicity disappears if \( z > 2 \text{ nm} \). The diagrams on the right show the different bending of the detached portion of the GNR in the forward (black) and backward (red) scans. The corresponding friction force loops are shown in fig. S16.

REFERENCES AND NOTES

ORGANIC CHEMISTRY

An aromatic ion platform for enantioselective Brønsted acid catalysis

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Chiral acid catalysts are useful for the synthesis of enantioenriched small molecules, but the standard catalysts require laborious and expensive preparations. Here, we describe a chiral Brønsted acid prepared in one step from naturally occurring (−)-menthol and readily available 1,2,3,4,5-pentacarbomethoxycyclopentadiene. Aromatic stabilization serves as a key contributing factor to the potent acidity of the resulting compound, which is shown to catalyze both Mukaiyama-Mannich and oxocarbenium aldol reactions with high efficiency and enantioselectivity. Catalyst loadings as low as 0.01 mole percent and preparative scalability (25 grams) are demonstrated. Alternative amide catalysts are also shown to be promising platforms. In addition to proton catalysis, a chiral anion pathway is demonstrated to be viable with this catalyst system.

Protonation dramatically alters the reactivity of a molecule. As such, Brønsted acid (proton donor) catalysts have long provided a potent strategy for the acceleration of a diverse array of chemical transformations (1, 2). In recent years, the invention of effective chiral Brønsted acid catalysts has enabled the development of numerous asymmetric reactions that furnish valuable chemicals in enantioenriched form (3–6). By and large, this area of enantioselective Brønsted acid catalysis has been dominated by the binaphthol (BINOL) phosphoric acid class of catalysts originally developed by Akiyama (7) and Terada (8). Although the utility of these catalysts is unquestionable, the major drawback to substituted BINOL-based catalysts is the lengthy, laborious, and expensive protocol required for their synthesis (9), which complicates catalyst optimization and limits their application on scale. Although alternative catalysts have been developed (10–16), the majority of these still rely on binaphthyl or other unnatural frameworks [e.g., VAPOL (17) or SPINOL (18)] as the basis of their chirality. This monocultural reliance on a single chiral scaffold is thus a major limiting factor for this important area of catalysis, and the identification of more readily accessible architectures is an important goal. Here, we describe a carbon acid platform for enantioselective Brønsted acid catalysis that uses aromaticity as its central acidifying element.

Although carbon acids typically manifest relatively high pKₐ values (where Kₐ is the acid dissociation constant), several structural modifications can substantially increase the propensity of C–H bonds to undergo ionization by stabilizing the anionic charge of the conjugate bases (19, 20) (Fig. 1A). The most common of these modifications involve σ-delocalization (induction) by electron-negative elements or groups and n-delocalization (resonance) by conjugated functionality. A third mode of carbanion stabilization involves a special form of resonance known as aromaticity, epitomized by the dramatic increase (10¹⁵) in acidity of cyclopentadiene versus its acyclic analog (21) due to the aromatic nature of the cyclopentadienyl anion. In the case of a 1,2,3,4,5-pentacarbonyxycyclopentadiene (PCCP) (1) (Fig. 1B), the three elements of induction, resonance, and aromaticity-induced acidification conspire to produce extremely strong carbon acids that rival the acidity of the mineral acids (22–24). In fact, the extended conjugation of such substituted cyclopentadienes is such that their acidic protons reside not on carbon but rather on oxygen as hydroxyluenes (compare 3) (25). With such strong acidity, we reasoned that PCCPs could serve as potent Brønsted acid catalysts and that ester or amide derivatives incorporating simple chiral alcohols or amines could offer synthetically accessible and effective enantioselective variants. Herein, we demonstrate the realization of this vision with the use of chiral PCCPs as highly efficient enantioselective Brønsted acid catalysts.

1,2,3,4,5-Pentacarbomethoxycyclopentadiene is readily available via the reaction of dimethyl malonate (4) and dimethylacetylene dicarboxylate (5) in pyridine-acetic acid, followed by treatment with potassium acetate (KOAc) to yield, after acidic workup, the acid 6 (26) (Fig. 2A). Compound 6 is a stable crystalline solid, and we have scaled this procedure to produce more than 50 g of this material. To access chiral derivatives, we found that refluxing 6 with excess (−)-menthol in the presence of N-methylimidazole in toluene furnished the pentamethyl ester 7 in 95% yield. Because (−)-menthol is a naturally occurring commodity chemical, we calculate that catalyst 7 can be prepared for about US$4/g (<$5.50/g for the unnatural enantiomer). As an alternative means to introduce chirality, we have also found that treatment of 6 with 1.0 equivalent of a primary amine (e.g., sec-naphthylamine) in refluxing toluene resulted in production of the corresponding monoamide product 8 in good yield. Because in the area of Brønsted acid catalysis, reaction rate has been shown to have a linear correlation with catalyst acidity (27), at least to a first approximation, we determined the pKₐ (CH₂CN) of both pentaester 6 (8.85 ± 0.05) and monoamide 9 (11.7 ± 0.1) and found that they compared quite favorably with known BINOL-phosphoric acids 10 (22–14) and other derivatives (Fig. 2B).

To evaluate the effectiveness of chiral PCCPs as enantioselective catalysts, we examined their performance in a Mukaiyama-Mannich reaction, which was known to be amenable to this type of asymmetric promotion (7) (Fig. 3A). We observed that 1 mole percent (mol %) of menthol-derived acid 7 catalyzed the addition of silyl ketene acetal 12 to imine 11 in ethyl acetate at −78°C in 1 hour to furnish the adduct 13 in 97% yield and 97% enantiomeric excess (ee). This result compares quite favorably to BINOL-phosphoric acid catalyst 14, which at 10 mol % loading was reported to catalyze the same reaction (in toluene) over 24 hours to furnish 13 in 98% yield and 89% ee. The loading of cyclopentadienyl catalyst 7 could be reduced to 0.01 mol % without compromising enantioselectivity. In terms of further catalyst screening, monoamides 8 and 15 were also found to induce appreciable enantioselectivity in this reaction, suggesting such catalysts may also be worthy of further development. Nevertheless, pentaester catalysts have thus far proven optimal.


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SUPPLEMENTARY MATERIALS

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