FRICTIONAL CHARACTERISTICS OF GRAPHENE AND ITS DERIVATIVES

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Summary Using friction force microscopy, nano-sacle frictional characteristics of graphene and fluorinated graphene were investigated. We found that a) friction of pristine grapheme depends on sample thickness with thinner sample giving higher frictional resistance; b) fluorination of graphene significantly increases its friction (roughly 10-fold). The unique mechanisms associated with these two unusual behaviours were discussed and the results revealed universal characteristics of friction of atomically-thin two dimensional materials.

INTRODUCTION

Recently, graphene and its derivatives have received vast attentions owing to their remarkable electronic, thermal, and chemical properties and are considered as key components for next-generation electronic devices. With the development of these atomically-thin materials, there is a pressing need to understand how such materials behave in contact because the ultra-high relative surface area renders adhesion, friction, and wear consequential for many critical applications in micro/nano-eletromechanical systems (M/NEMS). In this work, we systematically explored the frictional properties of pristine graphene (Gr) and fluorinated graphene (FGr) sheets deposited on various substrates using friction force microscopy (FFM). Since Gr and FGr are two-dimensional (2D) counterparts of common solid lubricants (graphite and fluorocarbon/Teflon), this study also provides an ideal opportunity to explore lubrication mechanisms at the nano-scale and may lead to discovery of new atomically-thin lubricants for M/NEMS devices.

FRICTION ON GRAPHENE AND FLUORINATED GRAPHENE

Experimental methods

Pristine graphene flakes were deposited onto SiO_2/Si substrates in ambient conditions using micro-mechanical exfoliation [1] as shown in Fig. 1(a). After deposition, the thinnest flakes were first identified using optical microscopy and the layer numbers of different areas were examined by contact mode atomic force microscopy (AFM) as well as Raman spectroscopy. The fluorinated graphene films were prepared by selectively etching large graphene films with XeF_2 gas in a Xactix etching system, as shown in Fig. 1(b). The large graphene films were obtained by growing graphene films on Cu foils via chemical vapour deposition and transferring them to SiO_2/Si substrates [2].
FFM was performed with a RHK UHV350 AFM in a dry nitrogen purged and subsequently sealed ultrahigh vacuum chamber. Friction force and topographic images were obtained simultaneously when an AFM tip scans over the sample flakes/films, as depicted in Fig. 1(c).

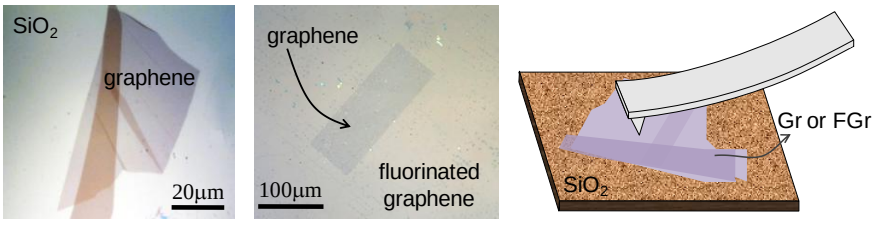

Figure 1. (a) Optical image of exfoliated graphene flake on SiO_2/Si substrate. (b) Optical image of graphene (darker area) and fluorinated graphene (brighter area) on SiO2/Si substrate. (c) A schematic showing the experimental setup: the samples are scanned by an AFM tip to measure their frictional properties.

Friction on pristine graphene

Fig. 2(a) is a friction force image of a graphene flake including four regions with different thicknesses. Friction measured on pristine few-layer graphene depended on sample thickness: thinner sample gave higher friction. This dependence is clearer when we plot energy dissipation per unit slip distance as a function of layer number as shown in Fig. 2(b). Energy dissipation (or friction) decreased monotonically with thickness and it levelled off for samples thicker than 5 layers. This observed trend was reproducible for various experimental conditions when graphene was deposited on SiO_2/Si substrate. However, when graphene was deposited on freshly-cleaved mica, it adhered strongly to the mica surface and the thickness dependence was absent. Combing the experimental observations with finite element simulations, we proposed [3] that the difference in the local out-of-plane deformation of the thin sheets when they interacted with the tip could account for the observed behaviour. Upon initial contact the thinner sheet puckers up and

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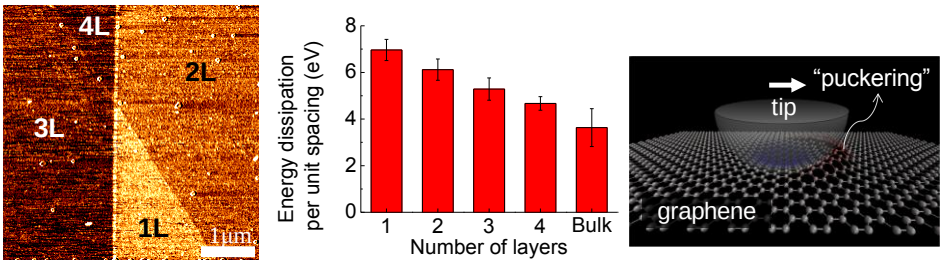
snaps to the tip due to adhesion. As the tip slides forward, the symmetry of the puckered configuration is broken due to friction and the thin sheet piles up more in front of the contact edge, as depicted in Fig.2(c). On the contrary, the puckering effect and piling up are significantly depressed for the thicker sheet because of its higher bending stiffness. The difference in puckering effect leads to different contact size and thereby different frictional resistance.

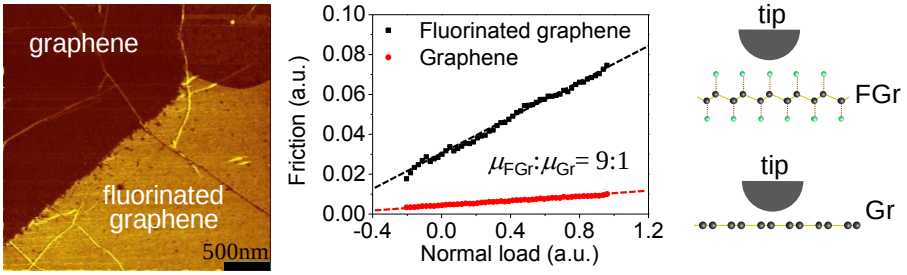


(a) (b) (c)

Figure 2. (a) FFM friction force image of the graphene flake including four different regions, 1L, 2L, 3L and 4L, corresponding to areas with 1-layer, 2-layer, 3-layer and 4-layer graphene; brighter color means higher friction. (b) Energy dissipation when the tip slips a unit graphene lattice distance; normal load was fixed at 5 nN. (c) A schematic showing a tip sliding over monolayer graphene with out-of-plane puckering effect.

Friction on fluorinated graphene

Friction on fluorinated monolayer graphene is much larger than that on pristine graphene under the same normal load, as shown in Fig. 3(a). Friction followed roughly a linear relationship with normal load for both materials and the coefficient of friction on FGr is estimated to be 9 times of that on Gr, as indicated by Fig. 3(b). The high frictional resistance on FGr is very surprising considering that bulk fluorocarbon has a very low surface energy (one third of graphite [4]) and has long been used a solid lubricant with very low friction. This is the first time that the drastically different frictional behaviour due to chemical functionalization of graphene has been was reported and the mechanism remained clearly understood to us. Nevertheless, we think that it is unlikely to be caused by the thin film puckering effect alone since the friction contrast is much more prominent than what we would expect. The atomic puckering of the backbone carbon atoms (converting from sp2 bonding to sp3 bonding) during fluorination or the extra dissipation originating from the terminating fluorine atoms may account for this unusual behaviour, as pictorially shown in Fig. 3(c). We are doing more experiments and carrying out atomistic simulations to further investigate this issue.



(a) (b) (c)

Figure 3. (a) FFM friction force image showing a boundary between graphene and fluorinated graphene; brighter means higher friction. (b) Friction as a function of normal load measured on graphene and fluorinated graphene; although both axes are not calibrated, the values of slope are directly comparable because the data were collected simultaneously. (c) A schematic an AFM tip scanning over fluorinated graphene (FGr) and graphene (Gr); FGr and Gr have different molecular structures.

CONCLUSIONS

Two unusual friction phenomena were observed for graphene and fluorinated graphene. We found that (a) friction on graphene weakly bound to substrates depended on its sample thickness; this could originate from the out-of-plane puckering effect when the thin films were under frictional contact; (b) fluorination of graphene increased its friction for almost one order of magnitude; this was likely caused by atomic puckering of the backbone carbon atoms or the extra dissipation from the terminating fluorine atoms. These results revealed a potentially universal characteristic of nano-scale friction for 2D materials as well as provided the first insights into the atomic-scale effects of functionalization on frictional properties of graphene.

References

[1] Novoselov K. S. et al.: Electric Field Effect in Atomically Thin Carbon Films. *Science* 306(**5696**): 666-669, 2004.

[2] Robinson J. T. et al.: Properties of Fluorinated Graphene Films. *Nano Letters* 10(**8**): 3001-3005, 2010.

[3] Lee C., Li Q. et al.: Frictional Characteristics of Atomically Thin Sheets. *Science* 328(**5974**): 76-80, 2010.

[4] Kita Y., N. et al.: Chemical Composition and Crystal-structure of Graphite Fluoride. *J. Am. Chem. Soc.* 101(**14**): 3832-3841, 1979.