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Impacts of the substrate stiffness on the anti-wear performance of graphene

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ABSTRACT
Owing to its excellent mechanical and tribological properties, graphene has been proposed to be a promising atomically-thin solid lubricant for engineering applications. However, as a typical two-dimensional (2D) material, graphene has an exceptionally high surface-to-volume ratio and is very susceptible to the surrounding environments. By performing nanoscale scratch tests on graphene deposited on four different substrates, we have shown that the anti-wear performance of graphene, characterized by the maximum load carrying capacity, is not an intrinsic material property. Instead, its value is significantly affected by the stiffness the substrates: Stiffer substrate typically results in a higher load carrying capacity. As revealed by finite element simulations, stiffer substrate can effectively share the normal load and reduce the in-plane stress of graphene by limiting graphene deformation, which enhances the overall load carrying capacity. In addition to the load sharing mechanism, the experimental results also suggest that the frictional shear stress during scratch tests may facilitate wear of graphene by lowering its equivalent strength. The deformation mechanism of graphene/substrate systems revealed in this work provides guidelines for optimizing the mechanical performance of 2D materials for a wide range of tribological applications.

Intrinsically strong mechanical strength and distinctively low friction render graphene an ideal ultra-thin lubricant for future mechanical applications. Recent studies combining nanoscale friction tests and molecular dynamics simulations have shown that graphene could withstand extremely high normal loads when scratched by diamond indenters. Because graphene has to be supported on a substrate when used as a lubricant, its deformation is naturally coupled with that of the substrate. For example, nano-indentation and friction experiment on graphene-covered Pt surface showed that graphene deformed simultaneously with the substrate. Due to the high stiffness and strength of graphene, the plastic deformation of the graphene-covered metal substrate could be significantly limited compared to the bare case. As the normal load originating from contact is carried by both graphene and the substrate, the deformability of the substrate may in turn affect the load carrying capacity of the composite system. To systematically explore this potential impact, we performed nanoscale scratch tests using an atomic force microscope (AFM) on monolayer graphene transferred on substrates of varying elastic stiffnesses. The experimental results confirm that the frictional shear stress during scratch tests may facilitate wear of graphene by lowering its equivalent strength. The deformation mechanism of graphene/substrate systems revealed in this work provides guidelines for optimizing the mechanical performance of 2D materials for a wide range of tribological applications.

For the experiments, monolayer graphene was grown on Cu foils by oxygen-assisted low-pressure chemical vapor deposition (CVD) and then transferred to target substrates using the wet transfer method, as illustrated in Fig. 1(a). Four types of substrates were adopted, including polydimethylsiloxane (PDMS), epoxy, SiO₂, and...
wafer, and sapphire disk. The PDMS substrate was prepared by mixing the pre-polymer base and curing agent (Sylgard184, Dow Corning) in mass ratio of 10:1. The epoxy substrate was prepared by mixing the A and B pre-mixture (Jinhua Electronic Materials Co., Ltd) in mass ratio of 2:1. The SiO$_2$ wafer (P type, Powerchip Technology Co. Ltd) and sapphire disk (SU001, TipsNano Co.) were used as purchased after alcohol cleaning. To improve the consistency and ensure a reliable comparison, the graphene samples were prepared using the same transfer technique from a same batch of CVD samples. Quality of the transferred graphene samples was inspected by Raman spectroscopy (Horiba HR800 with a laser wavelength of 514 nm), as shown in Fig. 1(b) and Fig. S1. The monolayer feature and the high quality of the transferred graphene samples were confirmed by the ratio of the 2D/G peaks and the absence of the D peak.

The nanoscale scratch tests were conducted with an AFM (Ntegra, NT-MDT Inc.) in ambient conditions (temperature around 20°C, relative humidity 20% ~ 40%). Two types of probes, CSC37/AL-BS (MikroMasch, nominal tip radius of 8 nm) and NSC16/AL-BS (MikroMasch, nominal tip radius of 8 nm), were used in the scratch tests. The normal and lateral spring constants of the probes were calibrated with the Sader’s method$^{19}$ and the diamagnetic lateral force calibrator,$^{20}$ respectively. As shown in Fig. 1(c), the scratch test was conducted by scanning the graphene sample within a rectangle region (typically 1 $\mu$m $\times$ 2 $\mu$m as indicated by the dashed rectangle) while gradually increasing the normal load until graphene failed.$^{14}$ The scan speed was set at 1 $\mu$m/s for all the scratch tests.

Fig. 2(a) shows the lateral force image of a graphene/PDMS sample collected under a relatively low load after it was subjected to two scratch tests within the regions highlighted by the dashed rectangles. During each scratch test, the normal load was gradually ramped from 4 nN to 118 nN. As indicated by Fig. 2(a), an obviously damaged zone with substantially high friction due to exposure of the underlying PDMS substrate can be found in each scratch region. To
quantify the critical normal load, we plotted the variation of friction with the normal load during the scratch tests as shown in Fig. 2(b). Initially, the friction force at relatively low normal loads stays at a low level (smaller than 10 nN), suggesting the integrity of graphene is maintained. However, when the normal load exceeds a critical value (∼59 nN in the present case), friction increases abruptly to a high value (larger than 100 nN) indicating the occurrence of graphene failure (more evidence can be found in Fig. S2). By tracking the normal load at the onset of graphene wear, we could determine the critical normal load for each scratch test. In this work, the critical loads were calculated as the averaged values from 5 sets of repeated scratch tests on different samples and the uncertainties were determined by the standard deviations.

In order to systematically explore the influence of substrate stiffness on load carrying capacity of graphene, we performed scratch tests for graphene deposited on three other types of substrates, i.e. epoxy, SiO_2, and sapphire. According to the friction evolution curves (shown in Fig. S3), the critical normal forces for graphene/epoxy, graphene/SiO_2, graphene/sapphire systems were determined to be 139 ± 15 nN, 3400 ± 1100 nN and 8300 ± 1600 nN, respectively. By plotting the critical normal force as a function of the Young’s modulus of the substrate in Fig. 2(c), one can clearly see that the load carrying capacity of graphene increases monotonically with the substrate stiffness. Since the roughness of substrate affects the mechanical properties of graphene in certain conditions, we calculated the roughness of the samples, and the root-mean-square (rms) roughness within a 0.5 μm × 0.5 μm area of the graphene samples on PDMS, epoxy, SiO_2 and sapphire are found to be 1.2 nm, 0.5 nm, 0.4 nm and 1.9 nm, respectively. Except for the case of sapphire, which has a higher roughness due to surface polishing, the roughnesses of different samples are roughly at the same level. Furthermore, since the variation of roughness is relatively random and does not match the monotonic trend of the critical load, we hypothesized that the observed behavior was unlikely to be primarily caused by roughness.

To better understand the influence of the substrate stiffness, finite element analysis (FEA) simulations were performed to analyze the deformation mechanism of the graphene/substrate system. In the FEA model, a rigid hemispherical indenter representing the AFM tip is pressed against an elastic substrate covered by an elastic thin sheet representing the graphene film, as schematically shown in Fig. 3(a). The interface between graphene and the substrate is assumed to be perfectly bonded throughout the simulations. Because the normal load during the scratch tests was typically very large (10s-1000s nN), we neglected the tip-graphene adhesion (on the order of a few nanoNewtons) in the model. The radius of the indenter was chosen to be 8 nm and the effective Young’s modulus, thickness and the Poisson’s ratio of graphene were set as 5500 GPa, 0.066 nm and 0.19, respectively, to correctly reproduce the in-plane and bending rigidities. The Young’s modulus and Poisson’s ratio were 2.57 MPa and 0.49 for PDMS, 2.34 GPa and 0.33 for epoxy, 73 GPa and 0.17 for SiO_2, 345 GPa and 0.29 for sapphire to match the experimental values (more information can be found in supplementary material). It is noted that the FEA model only simulated the normal indentation and no frictional sliding was introduced. This was based on the following considerations. First, the friction law between the tip and graphene is unclear and no generally accepted law has been proposed so far at the continuum level. Second, there is no existing criterion for failure of graphene when it is subjected to both in-plane stretching and surface shearing. Since the normal contact is often not strongly coupled with lateral sliding in contact mechanics problems, we adopted the normal indentation model as a first attempt. The potential impact of frictional sliding will be discussed later.

Previous atomistic simulations have suggested that bond breaking due to in-plane stretching is an important failure mechanism
for graphene wear during frictional sliding. In the FEA simulations, we recorded the variation of the maximum in-plane 2D stress inside graphene during indentation. As shown in Fig. 3(b) for the graphene/PDMS system, the in-plane 2D stress increases monotonously with the normal load. When the normal load increases to a critical value, denoted by $F_{CN}$, the in-plane 2D stress will reach the intrinsic strength of graphene $\sigma_s$, i.e. 42 N/m as reported previously. Based on this calculation, the critical normal load for the graphene/PDMS system can be determined to be 330 nN, as indicated by the red dashed line in Fig. 3(b). Following a similar procedure, we could obtain the critical loads for the other three systems (see more details in Fig. S4), which are plotted as red squared symbols in Fig. 3(c). Consistent with the qualitative trend in experiments, the predicted critical normal load increases with increasing substrate stiffness. This behavior can be understood as follows. Under the compressive normal load from the probe tip, both graphene and the substrate deform. Because graphene and the substrate surface are mechanically coupled (especially within the contact zone), their deformation is limited by the rigidities of both graphene and the substrate. For systems with stiffer substrates, the overall deformation of graphene and the substrate will be smaller under a same normal load, resulting in less in-plane strain in graphene (see more details in Fig. S5). Therefore, to produce a similar level of in-plane stress inside graphene, the systems with stiffer substrates have to be loaded with a larger normal force, exhibiting an enhanced load carrying capacity.

Despite the qualitative consistency in variation trend, all the critical normal loads predicted from the FEA predictions seem to be noticeably higher than the experimental values. We speculated that this disparity was due to the negligence of frictional shear stress in our model. In other words, the frictional shear stress during scratch tests might help lower the strength of graphene. To validate this idea, we performed nano-indentation tests without lateral sliding on the graphene/PDMS sample using the same AFM probe. Fig. 3(d) shows a typical indentation curve and the critical normal load from pure indentation without sliding is indeed significantly larger ($250 \pm 80$ nN, calculated from 4 sets of repeated experiments), which is now on a par with the theoretical predictions of perfect graphene ($\sim330$ nN). The difference in the critical normal load between scratch and pure indentation experiments on the graphene/PDMS samples suggests that the frictional shear stress indeed plays an important role in the failure of graphene. As far as we know, the effect of shear stress on mechanical strength of graphene has rarely been reported or discussed in literature and a full understanding may require a systematic study, perhaps with atomistic simulations. To qualitatively incorporate this particular effect, we assumed that the equivalent intrinsic strength of graphene was reduced to a lower magnitude, say $\sigma'_s$, due to the existence of shear stress. According to the theoretical curve shown in Fig. 3(b), the reduced 2D intrinsic strength of graphene $\sigma'_s$ can be estimated to be $17.4$ N/m by matching experimental data, as illustrated by the blue dash-dotted line. Using this reduced graphene strength, we could further predict the corrected critical normal load $F'_{CN}$ for the other systems (see Fig. S4 for more details). As shown by the blue triangles in Fig. 3(c), the corrected theoretical predictions fit well with the trend in experiments. The good consistency between simulations and experiments suggests that the load sharing mechanism from the substrate and the strength weakening due to frictional shear stress can well explain the substrate stiffness dependent wear behavior of graphene.

In summary, using AFM experiments and FEA simulations, we have shown that the anti-wear performance or the load carrying capacity of graphene is not an intrinsic property of graphene but critically depends on the substrate stiffness. Graphene on a stiffer substrate typically exhibits a higher load carrying capacity because its in-plane stress level is limited by the smaller deformation of the graphene/substrate system. Our experimental results also suggest that the friction shear stress during scratch tests may further facilitate the failure of graphene by lowering the equivalent intrinsic strength of graphene from the pure tensile strength. Our findings shed lights on the deformation mechanisms in graphene/substrate systems and offer some practical strategies for optimizing the anti-wear performance of 2D materials for mechanical applications.

See supplementary material for supported Raman spectra, AFM and FEA results.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 11772169, 11432008 and 11806761), National Basic Research Program of China (Grant No. 2015CB351903), the National Key Scientific Instruments and Equipment Development Project of China (61427901), and the State Key Laboratory of Tribology at Tsinghua University (Grant No. SKL.T2019B02).

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