Supporting Information

Scratching of Graphene-Coated Cu Substrates Leads to Hardened Cu Interfaces with Enhanced Lubricity

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1. Sample preparation and experimental procedures

Single layer graphene was deposited by traditional CVD method[1] on copper foil of which the thickness was 25 μm. The AFM (Cypher ES, Oxford Instrument) was used to examine the tribological characteristics of graphene under ambient conditions (temperature was 20 ℃ and relative humidity was around 30%) and dry condition for the environment tests (relative humidity was below 3% after the sample was heated in one hour and at 100 ℃ with dry N_2 continuously pumped in). The scratching tests, morphology characterization and the acquisition of force-distance curves were carried out with DLC coated AFM tip (NT-MDT, DCP11, A side). Normal force constant of the tip was calibrated by the noninvasive thermal calibration method described by Higgins et al[2] and the friction force was calibrated by wedge calibration method introduced by Ogletree et al [3] .

Raman microscopy (LabRAM HR800, Horiba) was used to characterize the thickness of and the quality of graphene under ambient conditions. The spatial resolution is 1 μm and the laser wavelength is 532 nm. Scanning electron microscopy (JSM-IT300) was used to characterize the wear of AFM tip.

The Cu substrate used in this study is multi-crystalline, and the surface type at each grain is different. The SEM and electron backscatter diffraction (EBSD, Mira3LMH, TESCAN) images of the Cu surface is shown in Fig. S1. For the scratching tests, AFM tip slides on the Cu surface within one grain. In other words, the sliding path never crosses a grain boundary. However, we've indeed carried out repeated experiments on different grains. The running-in behaviors found on different grains are similar.

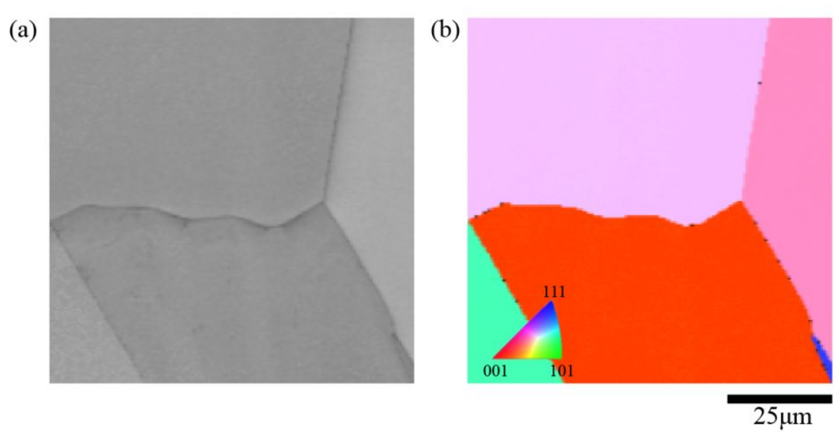

Figure S1. Surface type of the Cu substrate. (a) SEM image of the Cu surface. (b) Corresponding EBSD image shows the multi-crystalline structure.

2. Results of scratching test under dry condition

To investigate the effect of environmental contaminations, scratching tests on graphene/Cu were repeated in dry nitrogen atmosphere. At first, the sample was heated at 100℃ for 1 hr with dry N_2 continuously pumped in the environment chamber. The relative humidity was kept below 3%. The scratching tests were carried out (under 1.89 μN normal load)after the sample was cooled down to room temperature in dry nitrogen atmosphere. Similar running-in behavior is observed as shown in the friction vs cycle curve in Fig.S2(a). The friction map and height image of the surface after scratching is shown in Figs. S2(b) and (c).

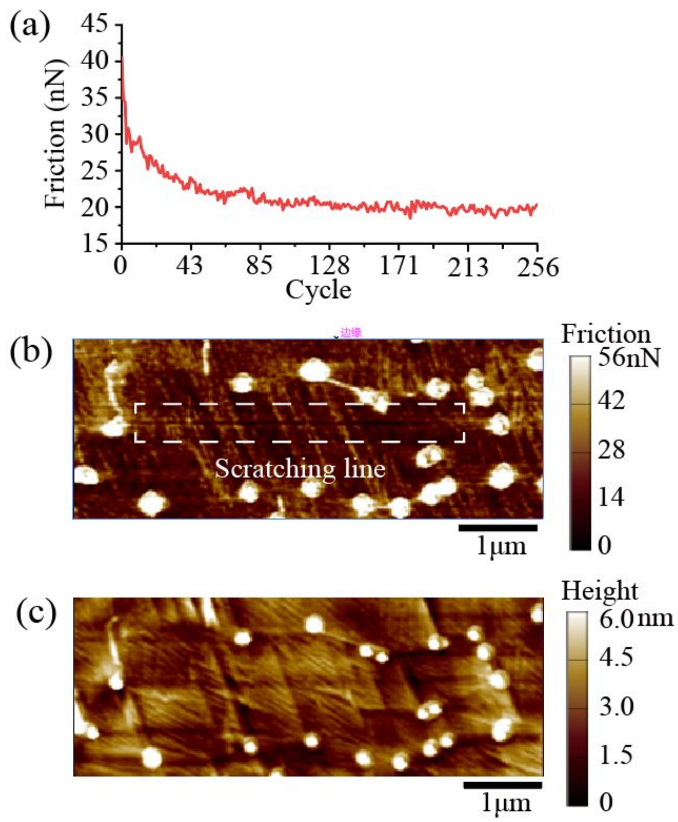

Figure S2. Results of scratching test under dry condition. (a) Evolution of average friction force during repeated line scratching. The friction image (b) and morphology(c) around scratching line by AFM after the line scratching test (obtained under 0.38 μN normal load).

3. Evolution of the average friction force during area scratching

The evolution of the average friction force was obtained from 12 square scratches on graphene/Cu, corresponding to Fig. 2e. The tendency of friction evolution was similar to line scratching tests.

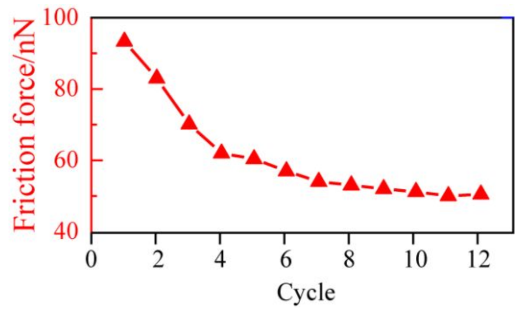

Figure S3. Evolution of the average friction force in Fig. 2e.

4. Topography change of graphene/Cu surface after line scratching tests

Topography change of the graphene/Cu sample surface is shown below. Fig. S4 (a) shows the topography (obtained under 0.94 μN normal load) after four parallel scratching tests (256 line scratches for each test with a typical normal load of 1.88 μN) on the graphene/Cu substrate. Dashed boxes indicate the positions where line scratches were carried out. Since the topography change is small compared to the ripples of Cu, the scratched lines are almost invisible in Fig. S4(a). To average out the influence of the ripples, the height profiles in the direction perpendicular to scratching direction are averaged, and shown in Fig. S4 (b). The four scratches corresponding to the dashed boxes are evident, indicated by the numbers 1 to 4, and the plastic deformation of the substrate after line scratching tests is found around 0.5 nm**.**

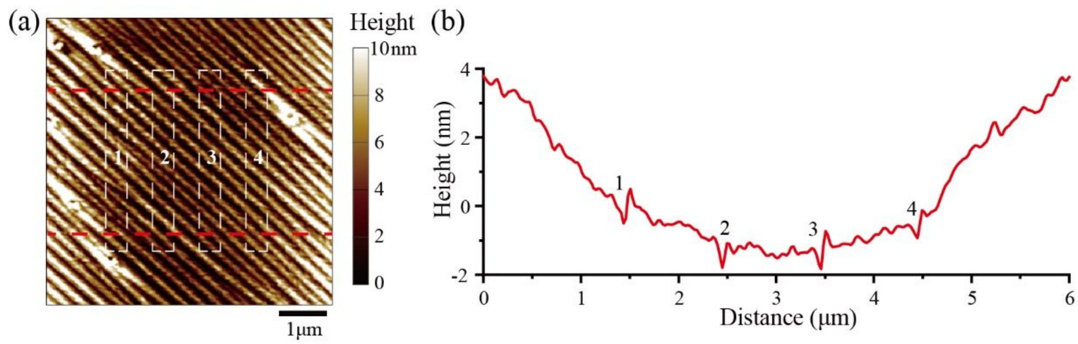

Figure S4. Topography change of the graphene/Cu sample surface after line scratching tests. (a) The topography after four same line scratching tests (in white dashed box, 256 line scratches with a typical normal load of 1.88 μN) and surrounding area. (b)The average height evolution of vertical direction between red dashed lines in (a). The horizontal axis (Distance) is along red lines in (a).

5. Topography and friction characterization of the graphene/Cu substrate after area scratching

A more detailed friction and topography analysis of the graphene/Cu substrate (in Figs. 2(e) and (f)) after area scratching is shown below. In Fig. S5 (a), the average friction over the scratched and unscratched domain is 21.2±7.8 nN and 30.2±6.9 nN, respectively. In Fig. S5 (b), the as-prepared graphene/Cu sample has a relatively large original roughness of 16.24 nm, with about 60 nm deep trenches. The plastic deformation of Cu is likely too small to detect, when compared to the large roughness. Figs. S5 (c) and (d) are the partial enlarged images of blue dashed box in (a) and (b), respectively. The friction profile along the red line in Fig. S5(c) is shown in Fig. S5(e). The average friction of scratched and unscratched parts on the line is 1.1±0.6 nN and 13.5±1.2 nN, respectively.

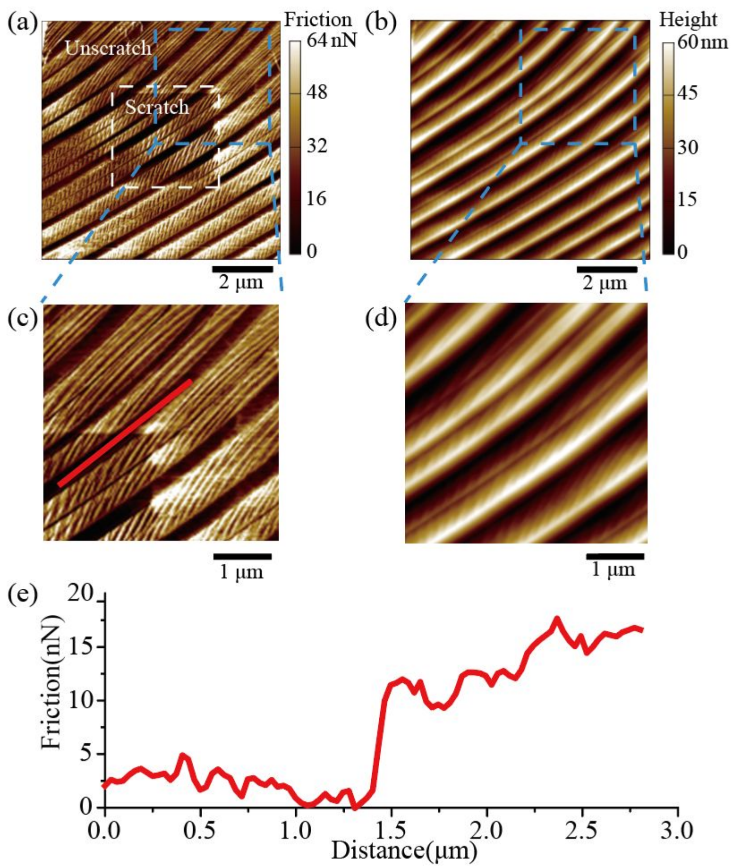

Figure S5. Topography and friction characterization of the graphene/Cu substrate after area scratching. (a) AFM friction image of the graphene surface after 12 area scratches. (b) Height image of the graphene surface after 12 area scratches. (c) and (d) The partial enlarged images of blue dashed box in (a) and (b), respectively. (e) The friction profile of red line in (c).

6. Topography change of the bare Cu sample surface after line scratching

After line scratching on bare Cu substrate in Fig. 3(c), the friction and height images obtained under 0.087 μN are show below. In Fig. S6 (c), the height profile along the red line in Fig. S6 (b) shows a 14 nm deep scratch caused by the wear of Cu. This result shows that, different from graphene/Cu, the bare Cu substrate is worn significantly during scratching tests.

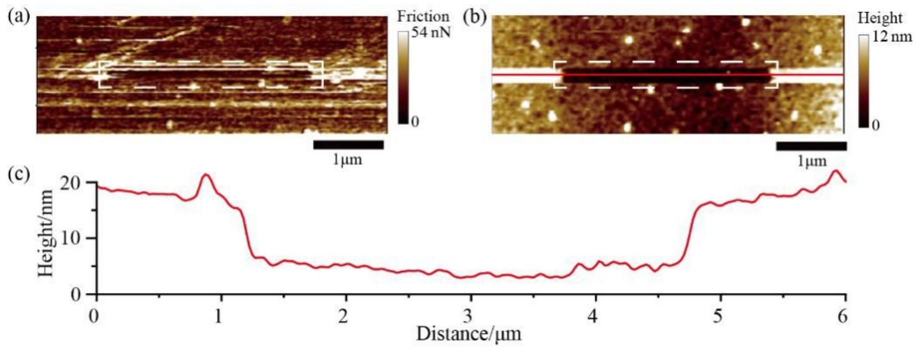

Figure S6. Topography change of the bare Cu sample surface after line scratching. (a) Friction map of the surface after scratching. (b) Height image of the surface after scratching. (c) Height profile along the red section line in (b), a 14 nm deep scratch is found on the bare Cu surface.

7. Scratching tests on graphene/SiO_2

To further support the hardening mechanism, line scratching tests were also conducted on graphene/SiO_2 substrate with AFM tip of the same type (DCP11). The normal load is 1.56 μN (similar to typical normal load for graphene/Cu, 1.88 μN). The friction vs cycle curve is shown in Fig. S7. No running-in behavior is found. This is possibly due to that SiO_2 is more brittle than Cu and thus is less hardened during repeated scratching[4-5].

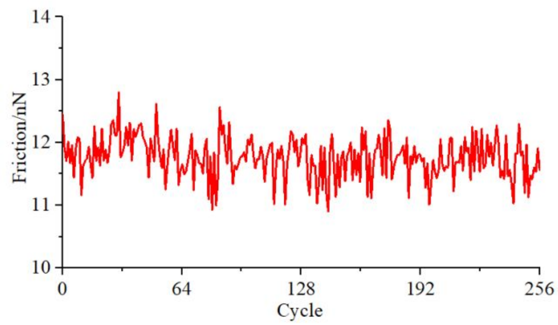

Figure S7. The friction vibration during line scratching on SiO_2/Si substrate with graphene coated by AFM.

8. Running-in at different locations

The friction vs cycle curves at two locations during a line scratching test are plotted in Fig. S8, for a line scratching test (Figs. 1(c) and (d)). The results show that the running-in behavior at different location is similar. And the number of cycles needed for steady state is almost the same.

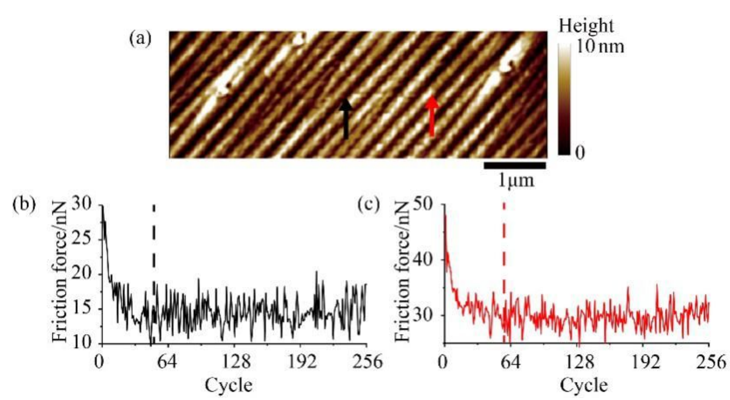

Figure S8. The friction vibration during line scratching on Cu substrate with graphene coated by AFM. (a) The height image of Fig. 1 (d). (b) and (c) are the local friction evolution indicated by black and red arrows in (a), respectively.

Reference

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