Electronic Supplementary Material (ESI) for Nanoscale

SUPPLEMENTARY INFORMATION

Effect of surface morphology on friction of graphene on various substrates

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Sample preparation and identification of thickness

To deposit graphene sheet simultaneously onto both h-BN and SiO_2 substrate, we chose the micromechanical cleavage method[S1] of single crystalline bulk source materials purchased from Momentive Performance Materials (h-BN source) and Covelant Materials (graphite source). Before the deposition of the materials the SiO_2 substrate was cleaned using piranha (H2SO4+H2O2) for several hours. The thickness of thermally grown oxide was approximately 300 nm. Any further treatments were not done after deposition, so almost pristine materials were used for the measurements. We found thin graphene layers optically (Fig. S1) and determined the number of graphene layers with Raman spectroscopy and atomic force microscopy (AFM) (Fig. S2). The graphene 2D peak at ~2700cm^{-1} and h-BN peak at 1366 cm^{-1} represent mono- and bi-layer graphene and bulk h-BN, respectively.[S2,S3] Penta- and hexa-layer graphene were ascertained by thickness measurement using AFM in tapping mode. The thicknesses of h-BN and bulk-like graphene, which was used as the flat substrate for graphene, were typically a few tens of nanometers and highly flat compared to SiO_2 surface. In the case of graphene on bulk graphite, we scanned the region where graphene sheets looked like to be placed onto bulk graphite using AFM and checked whether graphene sheets were deposited onto bulk graphite or not (Fig. S3). To prepare folded graphene samples, we scratched graphene edges repetitively using an ultrasharp AFM tip (NT-MDT, NSG01 DLC). In this step, applied load (1 to 5 nN) and scanning speed (10 to 40 μm/s) were varied until folding event occurred (Fig. S4).

AFM and FFM measurements

An E-sweep (Environment Control Unit) manufactured by Seiko Instruments was used to characterize topography and to perform FFM test in an ambient environment (25 to 50%

relative humidity, 20 to 25℃). A sharp Si tip (Seiko, SI-AF01) was used in micro-scale test. 1 nN of applied load was selected and 0.5 Hz scanning was kept for each scan area to obtain clean images. There was little variation of the friction measurement results for different scan speeds, thus little speed dependence.

We compared magnitude of graphene friction with different substrates without lateral force calibration of AFM cantilever (Fig. S5). A friction force exerted at the apex of the atomic force microscope (AFM) tip during scanning will cause torsion of the cantilever in friction measurement, and then deflection angle difference of the laser beam received in the photodetector would be identified. Without lateral force calibration, therefore, the friction signals taken from different areas can be simultaneously processed and compared qualitatively and quantitatively.

By employing amplitude-modulation AFM in the non-contact mode with Si AFM tip (Budge Sensors, Tap300Al-G, Resonant Frequency 300 kHz), we characterized graphene topography. The standard deviation of height distribution was chosen for representing the roughness of the surface.[S4] Our topographic images did not go through any filtering or smoothing process. We compensated bow and tilt in the AFM images with a third-order line and flattening process. For analyzing the topographic images, area of 500 X 500 nm^2 was consistently scanned with scan speed of 0.4 Hz for each sample. Based on the measured heights, we drew histograms and computed the standard deviation of it.

In the case of a graphene on h-BN substrate (Fig. S6), there is no friction force difference between the two areas with different thicknesses.

As shown in Fig. S7, for graphene on SiO_2, the lattice look distorted and the lateral period of the lattice looks slightly larger because of out-of-plane deformation of graphene. This does not happen in graphene on h-BN because of no puckering effect.

Fig. S8 shows AFM and FFM images of graphene sheets at which we could observe folded and unfolded regions simultaneously. We obtained almost equal magnitude of friction for folded and unfolded graphene. From insets of AFM images for characterizing graphene topography (Fig. S8), we found that folded graphene roughness reflected surface morphology before folding event.

To verify small height difference between ripple of folded graphene and the flat bilayer, we acquired topographic images of bi-layer graphene and folded monolayer graphene right beside mono-layer graphene (Fig. S9). Schniepp et al. measured size of a small gap between the ripple formed by upper and lower layer originating from finite intrinsic stiffness of graphene.[S5] They found that the gap existed in all of folded region (longer than 30 nm) by means of AFM. However, we could not find such a gap occupying entire sub-surface and thus our speculation for the friction mechanism of folded graphene due to the gap cannot account for our results.

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(S4) C. H. Lui, L. Liu, K. F. Mak, G. W. Flynn, T. F. Heinz, Nature, 2009, 462, 339-341

(S5) H. C. Schniepp, K. N. Kudin, J.-L. Li, R. K. Prud'homme, R. Car, D. A. Saville, I. A. Aksay, ACS Nano, 2008, 2, 2577-584

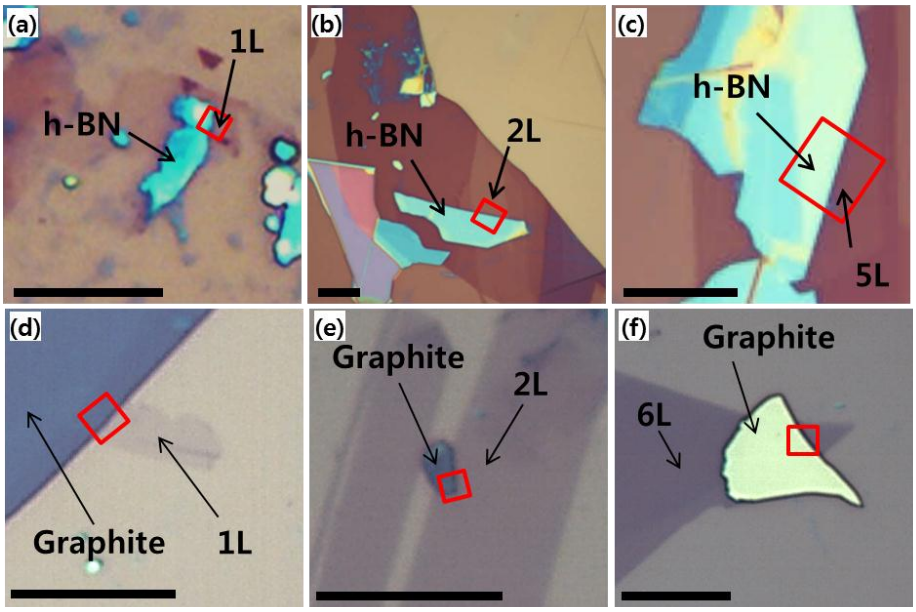

Fig. S1 Optical images of graphene on h-BN and SiO2 (a,b and c) and graphene on bulk-like graphene and SiO2 (d,e and f). The red square represent AFM scan area shown in figure 2 in main text. Forward friction images were measured by AFM. 1L, 2L , 5L and 6L indicate mono-, bi-, penta- and hexa-layer graphene, respectively. Scale bars, 10 μm.

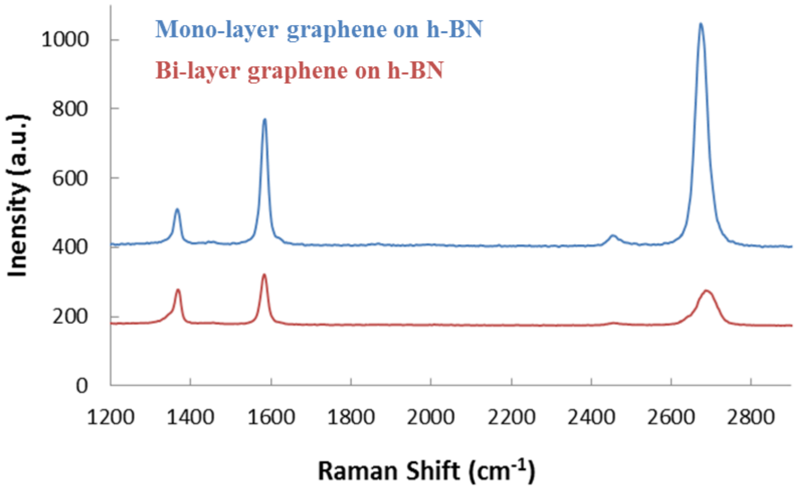

Fig. S2 Raman spectra of mono-layer graphene on h-BN. The graphene 2D peak at ~2700cm^{-1} and h-BN peak at 1366 cm^{-1} represent mono-layer graphene and bulk h-BN, respectively.

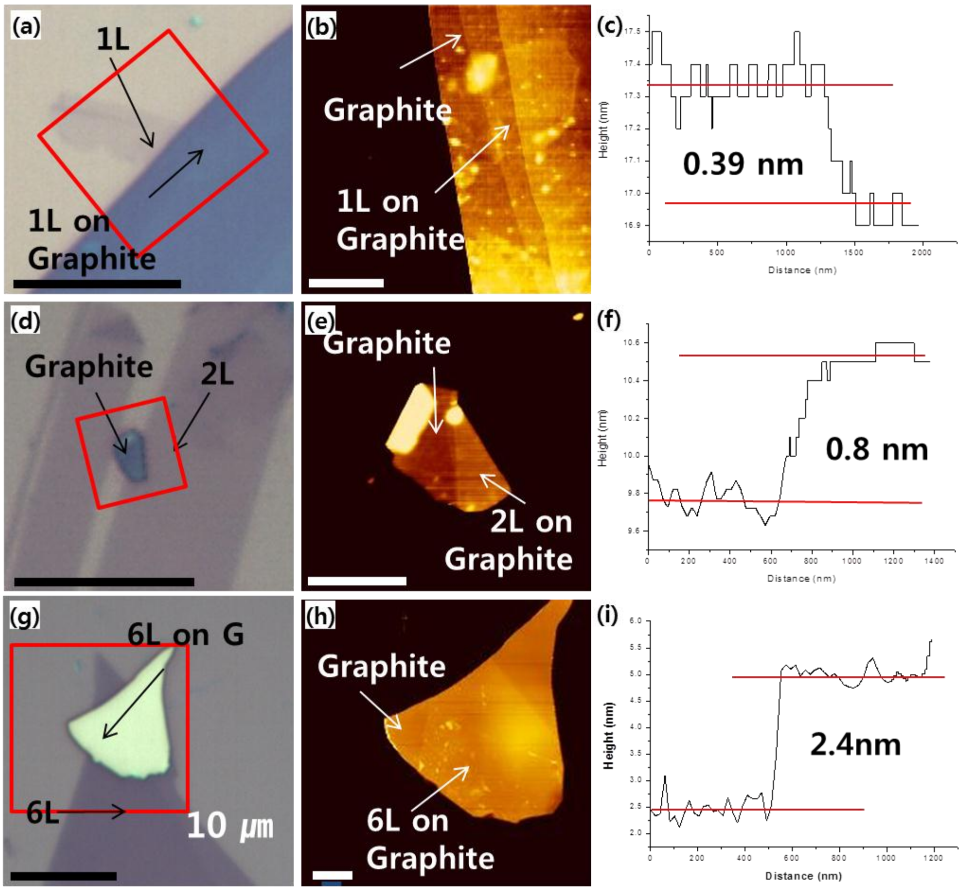

Fig. S3 Optical images, friction images and thickness of mono-layer (a, b, and c), bi-layer (d, e, and f), and hexa-layer (g, h, and i) graphene on bulk-like graphene. The red square represent AFM scan area. Black scale bars, 10 µm. White scale bars, 2 µm.

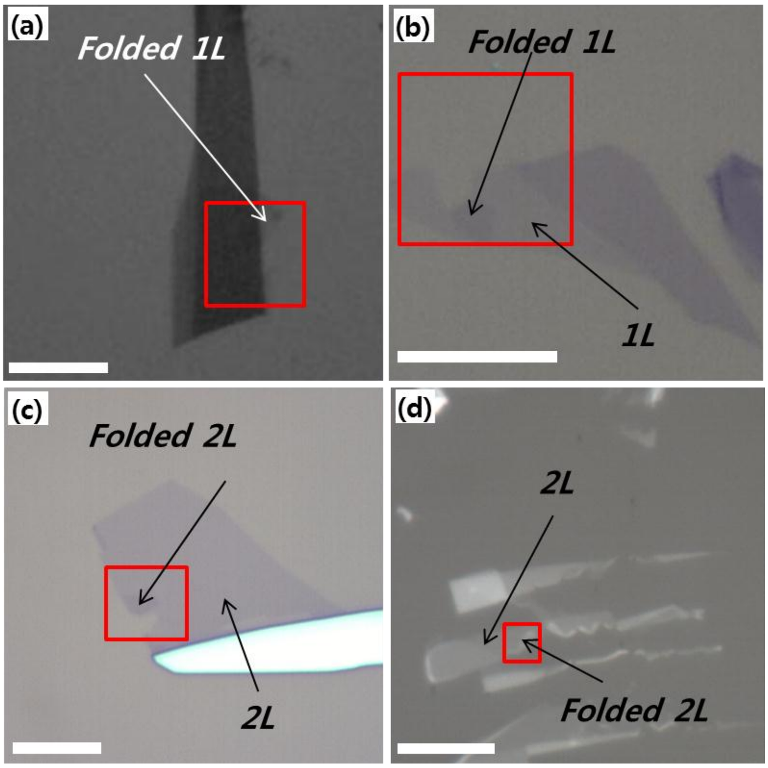

Fig. S4 Optical images of folded (a and b) mono-layer graphene on SiO2, (c) bi-layer graphene on SiO2 (d) and mono-layer graphene on mica. Red square indicates AFM scan area. Scale bars, 10 μm.

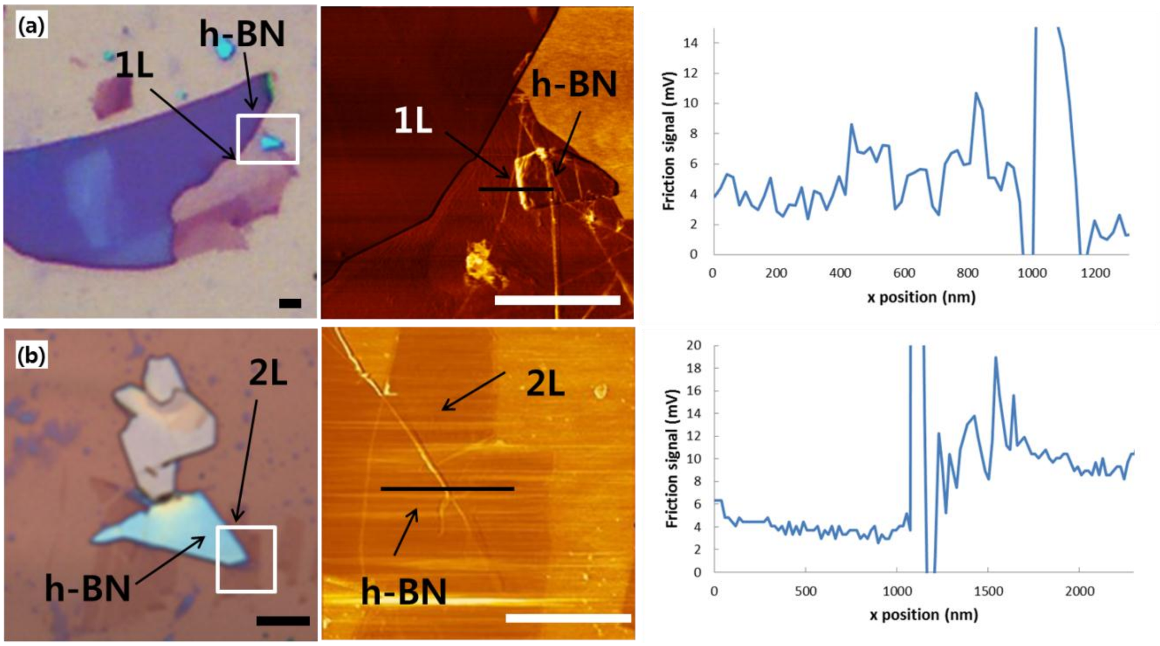

Fig. S5 Optical images, friction images and profiles of friction force along the black scan-lines. (a) mono-layer graphene and (b) bi-layer graphene on h-BN. Black scale bars, 5 μm. White scale bars, 2 μm

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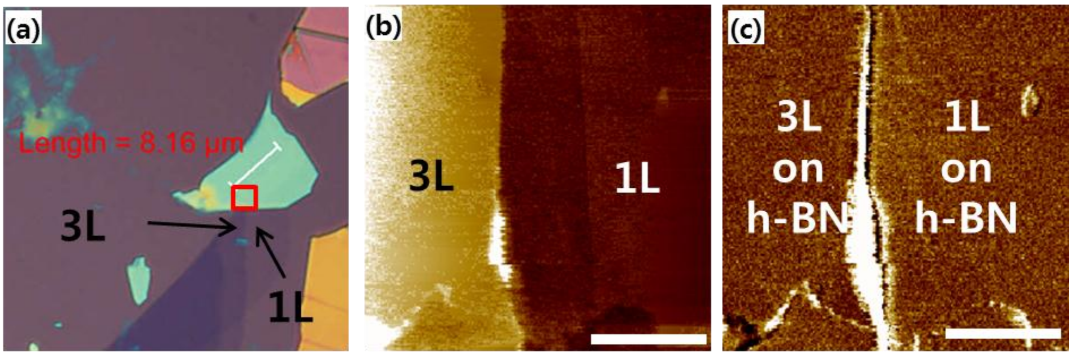

Fig. S6 Optical and AFM images of graphene on h-BN. (a) Optical microscope image. The red square represent AFM scan area. (b) Topographic and (c) forward friction images of graphene on h-BN measured simultaneously by AFM. Scale bars, 0.2 μm.

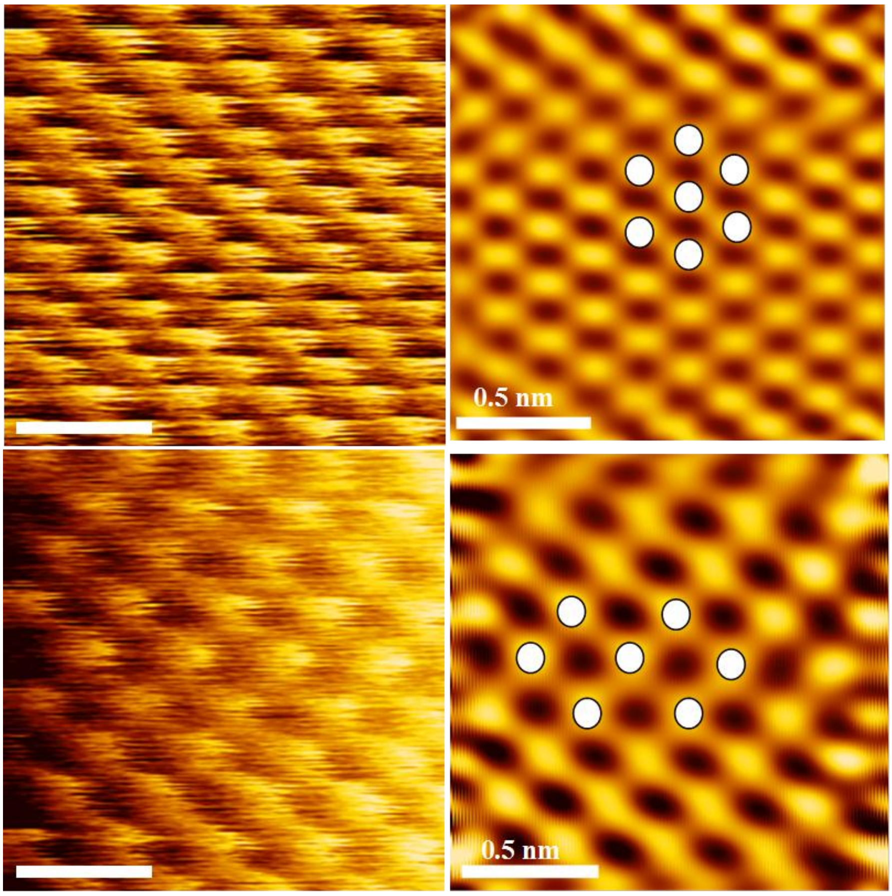

Fig. S7 Raw (left) and low-pass filtered (right) images showing the friction signal in the forward sliding direction for mono-layer graphene on h-BN (upper) and mono-layer graphene on SiO_2 (lower) samples. The filtered images show the periodicity of the lattice; white dots represent the periodic sites of the friction force signal. For graphene on SiO_2, stretched lattice can be clearly seen. Scale bars, 0.5 nm.

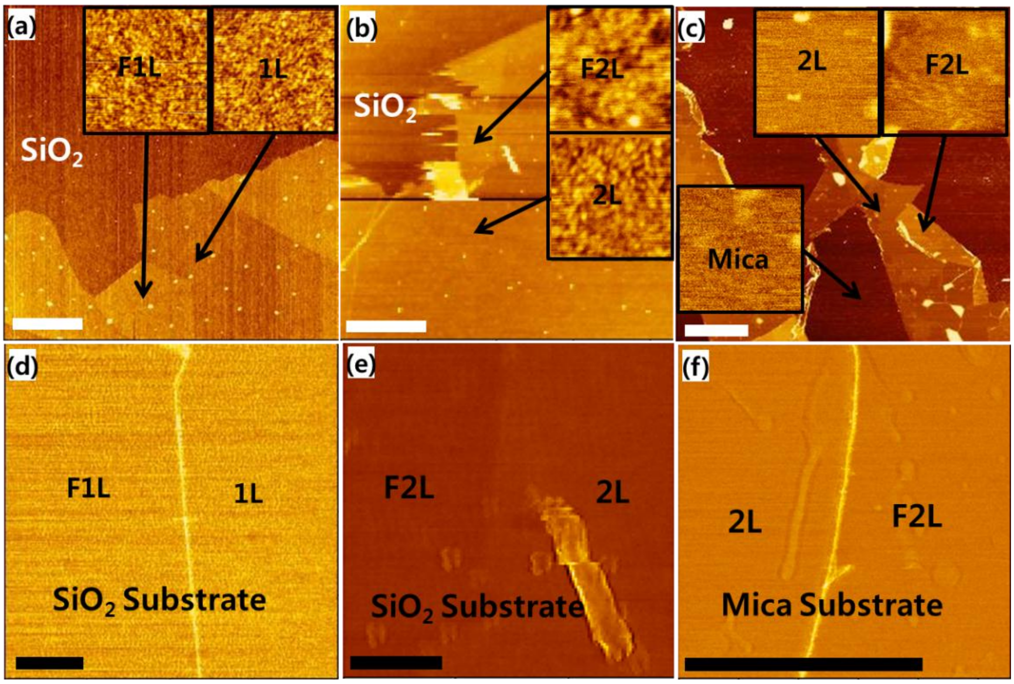

Fig. S8 AFM images of (a) folded mono-layer graphene on SiO_2, (b) folded bi-layer graphene on SiO_2 substrates (c) and folded mono-layer graphene on mica. FFM images of (a) folded mono-layer graphene on SiO_2, (b) folded bi-layer graphene on SiO_2 substrates (c) and folded mono-layer graphene on mica. Inset images acquired for the region indicated by black arrows have same scan size of 500 X 500 nm^2 with identical z-scale (0 to 1.23 nm). White scale bars, 2 μm. Black scale bars, 400 nm.

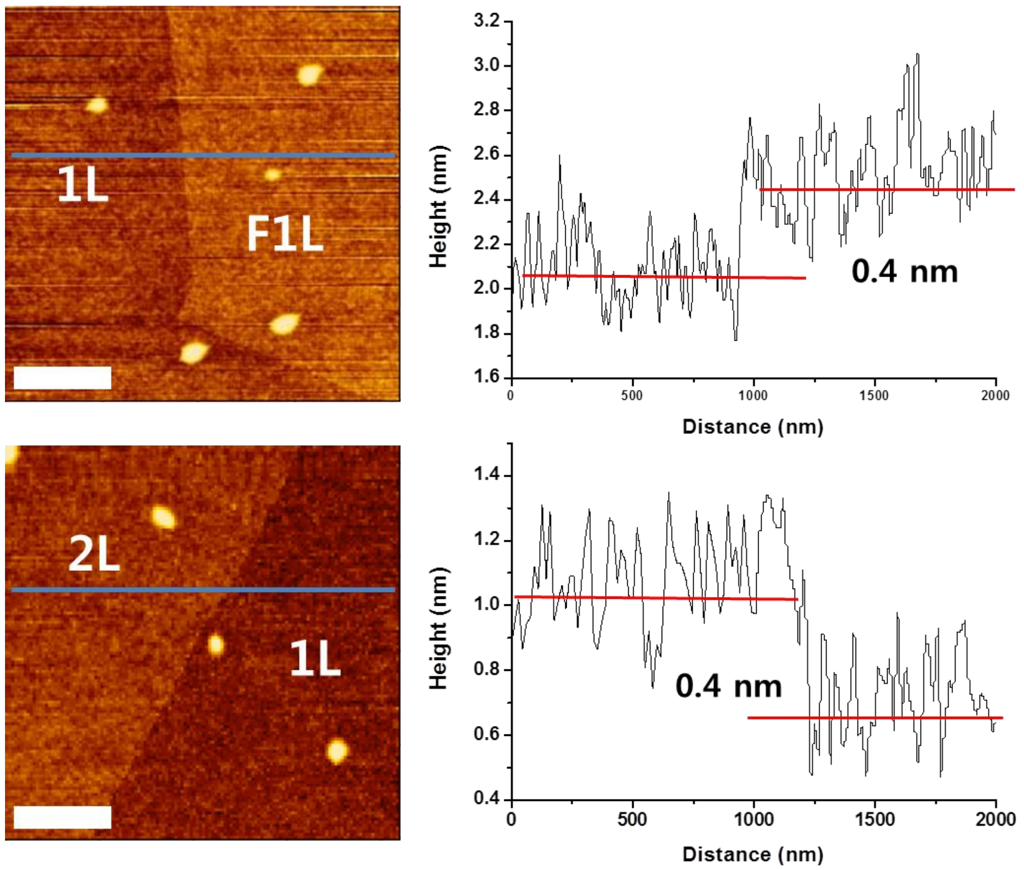

Fig. 9 AFM image of (a) unfolded and folded mono-layer graphene on SiO2 (b) height profile along blue line in (a). AFM image of (c) mono- and bi-layer graphene. (d) height profile along blue line in (c). Scale bars, 500 nm.