Master thesis

Assessment of wear resistance of single layer h-BN, MoS_2, and graphene using colloidal probe atomic force microscope

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Assessment of wear resistance of single layer h-BN, MoS_2, and graphene using colloidal probe atomic force microscope

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ABSTRACT

Assessment of wear resistance of single layer h-BN, MoS_2, and graphene using colloidal probe atomic force microscope

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Two-dimensional materials such as single layer hexagonal boron nitride (h-BN), molybdenum disulfide (MoS_2) and graphene have widely investigated because of their outstanding mechanical characteristics, chemical inertness and thermal stability. Furthermore, single layer h-BN, MoS_2, and graphene also shown extremely low friction characteristics and strongly adhere to the substrate that make these thin films as potential candidates for protective coating layers and solid lubricants at micro and nano-scales. In this work, a systematical investigation of surface damage characteristics of single layer h-BN, MoS_2, and graphene were carried out using atomic force microscopy colloidal probe in the long-term test. The findings in this work may be helpful to give a better understanding of the surface damage characteristics of single layer h-BN, MoS_2, and graphene. And this work may be useful to suggest single layer h-BN, MoS_2, and graphene as protective coating layers and solid lubricants to significantly prolong the operational lifetime of micro- and nano-devices.

1. INTRODUCTION

1.1 Background and motivation

In micro- and nano-devices, surface reliability is one of the critical issues. It is found that the surface damage will give a dramatic effect on the performance as well as the operational lifetime of systems, especially in micro- and nano-devices where dimension and space between parts are extremely limited. Therefore, studying materials for protective coating layers to enhance the operational lifetime of mechanical systems is always an attracted research area. At micro- and nano-scale, conventional protective coating layers make a considerable thickness on the coated systems and these coating layers could make the change of geometry and desired properties of systems. Therefore, it is essential to propose protective coating materials which can protect the contacting surfaces without changing the geometry, maintain the desired properties and strongly adhere [1] to the substrate of the micro- and nano-systems. With these requirements, two-dimensional materials such as hexagonal boron nitride (h-BN), molybdenum disulfide (MoS_2), and graphene are proposed as promising candidates.

Since the first atomically layered material which possesses excellent properties has been reported [2], atomically thin materials such as h-BN, MoS_2, and graphene have still attracted much attention because of their remarkable mechanical properties and flexibility [3-5]. For instance, the high elastic modulus of single layer h-BN, MoS_2, and graphene has been reported ~ 865, 270, and 1000 GPa, respectively [5-7]. Thus, this property helps to recognize these are relatively strong materials, especially single layer graphene, which is reported as the strongest material ever measured. In addition, single layer h-BN, MoS_2, and graphene also show extremely low friction characteristics [8-14], chemical inertness, and thermal stability [15,16]. Moreover, it was found that these atomically thin films of h-BN, MoS_2, and graphene strongly adhere to the substrate [17]. Owing to these outstanding properties, single layer h-BN, MoS_2, and graphene have been proposed as potential candidates for protective coating layers solid lubricants in micro- and nano-devices.

In various studies, nanoscale wear of single- and few-layer h-BN, MoS_2, and graphene has been investigated using AFM and the outcome indicated that atomically thin h-BN, MoS_2, and graphene are only failed under extremely high contact pressure from 2.52 to 9.34 GPa [17-21]. The effect of environments and the edges of graphene on mechanical and tribological properties of these materials has also reported in other studies [22-24]. These studies usually use a sharp atomic force microscopy (AFM) tip with small tip radii from about 2 to 40 nm corresponding to high contact pressure up to 9.34 GPa [17,19] that made extremely high conditions to completely fail these thin films immediately. However, surface damage characteristics of single layer h-BN, MoS_2, and graphene under larger tip radius (e.x colloidal probe with the probe radius of 6 – 8 micrometers) and lower contact pressure (under 1 TPa) in long-term test remains unexplored yet. Therefore, it is necessary to understand the surface damage characteristics of single layer h-BN, MoS_2, and graphene in the long-term test in order to propose these materials to protective coating layers to prolong the operational lifetime of micro- and nano-devices.

1.2 Objective of the thesis

The objective of this research is to systematically investigate the wear resistance of single layer h-BN, MoS_2, and graphene based on reciprocating scratch test using a silica AFM colloidal probe. The silica AFM colloidal probe is kept sliding against specimens under a contact pressure below 1 GPa in long-term test (up to 1 million cycles) to observe the surface damage characteristics of specimens. The outcome of this work may give a better understanding the nanotribological properties of single layer h-BN, MoS_2, and graphene to propose these thin materials to protective coating layers and solid lubricants for micro- and nano-devices.

2. EXPERIMENTAL DETAILS

2.1 Specimens preparation and characterization

In this work, single layer h-BN, MoS_2, and graphene were prepared by mechanically exfoliation method from their bulk h-BN (HQ Graphene), MoS_2, and graphite (SPI Supplies) and deposited onto the silicon substrate with 285 nm silicon dioxide (SiO_2) capping layer. This was a simple and effective method to peel off single layer h-BN, MoS_2, and graphene from their bulk materials. Firstly, a piece of the natural flake was taken and put on the adhesive-side of tape. Then the top of the tape was taken and gently pulled it apart from the bottom. The second piece of tape was used to peel a few layered materials off from the first piece of tape. This process was continued about 10-12 times in order to observe thin enough of this flake. Then the tape with thin sheets of h-BN/ MoS_2/ graphene was stuck onto the SiO_2/Si substrate and peeled it away. Some specimens of single and few-layers h-BN, MoS_2, and graphene were deposited onto the SiO_2 substrate. Fig. 1 shows (A) thin flake of exfoliated graphene on the adhesive-side of the tape before deposited and (B) SiO_2/Si substrate glued on a glass slide. After deposited onto SiO_2 substrate, the locations of specimens were identified in the next step.

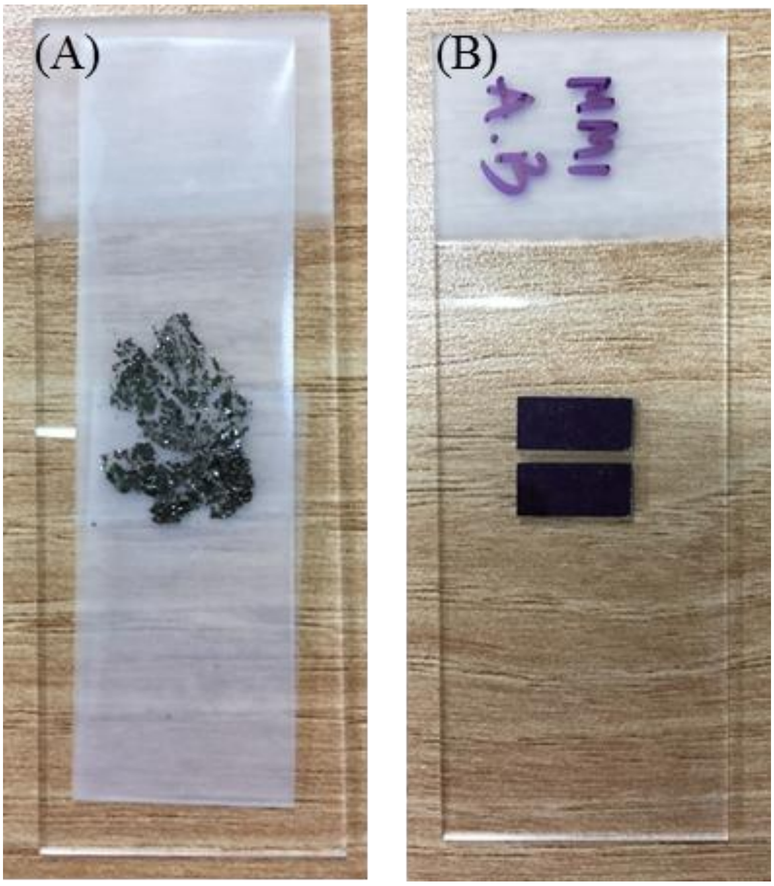

Figure 1. (A) Example of thin flakes of graphene specimens on scotch tape and (B) SiO_2/Si substrate glued on a glass slide.

Single layer h-BN, MoS_2, and graphene were then viewed and identified with a confocal microscope (VK-X200, Keyence) due to the optical contrast difference between specimens and SiO_2 substrate. AFM intermittent contact mode (MFP-3D, Asylum Research) was then employed to characterize the topography and determine the thickness of single layer h-BN, MoS_2, and graphene specimens. A sharp silicon cantilever (tip radius of 9 ± 2 nm) with a nominal spring constant of 2 N/m (AC240TS, Olympus) has been used to characterize the thickness of specimens.

After specimens was characterized by AFM intermittent contact mode, Raman spectra (Alpha 300R, Witec) were then used to determine the characteristic peaks of single layer h-BN, MoS_2, and graphene and to confirm the number of layers of the specimens. The laser excitation wavelength of 532 nm (1.4 cm^{-1} spectral resolution) was used in this experiment. And the 100× objective which has a laser spot size of about 720 nm was used with a grating of 1800 lines/mm in order to collect the spectra. To minimize the effect of laser-induced particles and thinning effect on the topography and mechanical properties of specimens, especially for single layer MoS_2 specimens [25-27], the laser power was set at 0.5 mW for 10 s to collect the spectra. The specimens were put in a dark chamber during the Raman measurement to eliminate the effect of ambient light source [28].

2.2 Reciprocating scratch test using AFM

The reciprocating scratch test of single layer h-BN, MoS_2, and graphene has been systematically conducted using AFM colloidal probe after the preparation and characterization of specimens. The silica micro-sphere (Polysciences, Inc.) with a relatively high hardness and relatively good surface [29] was chosen and attached to the free end of an AFM cantilever as described in the previous studies [30,31]. To determine the dimensions of the silica colloidal probe, confocal microscope and scanning electron microscope (SEM, JEOL JSM 5800, Japan) were used. Topographic image of the contact area of the silica colloidal probe before and after reciprocating scratch test was characterized by AFM intermittent contact mode. It was found that the silica sphere, which has a radius from 6 to 8 µm, can provide an appropriate contact pressure (under 1 TPa) for the long-term test. In this work, the colloidal probe with a relatively smooth surface and a probe radius of ~ 7 µm was used to scratch the surface of single layer h-BN, MoS_2, and graphene specimens. Fig. 2 shows the confocal microscope image and SEM image of a colloidal probe used in this experiment.

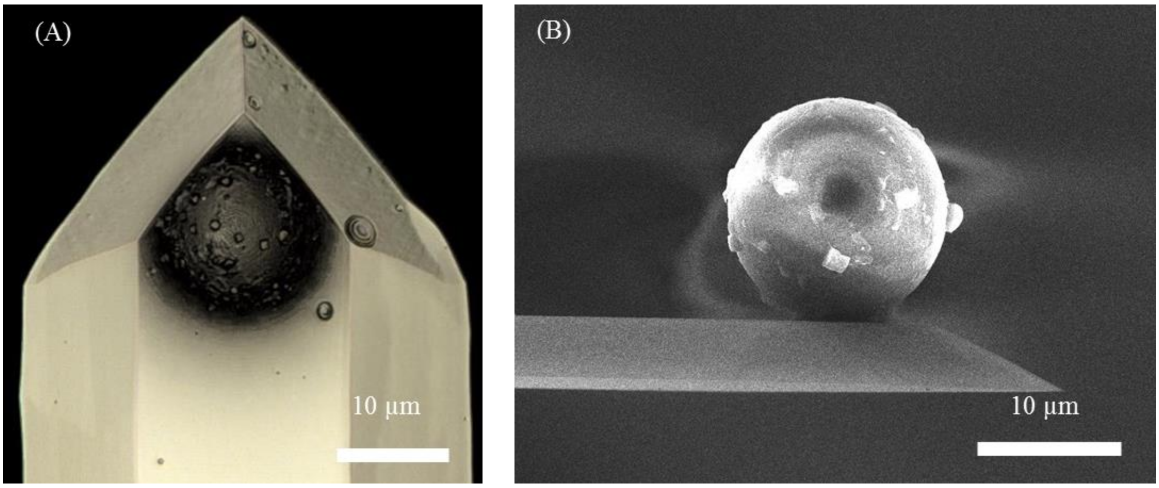

Figure 2. Example of (A) confocal microscope image and (B) SEM image of a colloidal probe.

After characterization of the colloidal probe, the reciprocating scratch test has been conducted by continuous sliding colloidal probe against the specimens. Fig. 3 shows a schematic illustration of a reciprocating scratch test of single layer h-BN, MoS_2, and graphene specimens using AFM colloidal probe. The colloidal probe was kept to continuously slide against the specimens during the reciprocating scratch test. Various normal forces which range from 10 to 70 µN were applied to the colloidal probe to scratch the film on a track of 1 µm with a constant speed of 40 µm/s. The variation of friction force is monitored during the reciprocating scratch test. And the test is conducted until the failure of specimens or stopped after 1 million cycles. It took about 18 hours for 1 million cycles reciprocating scratch test with a frequency of ~ 16 Hz.

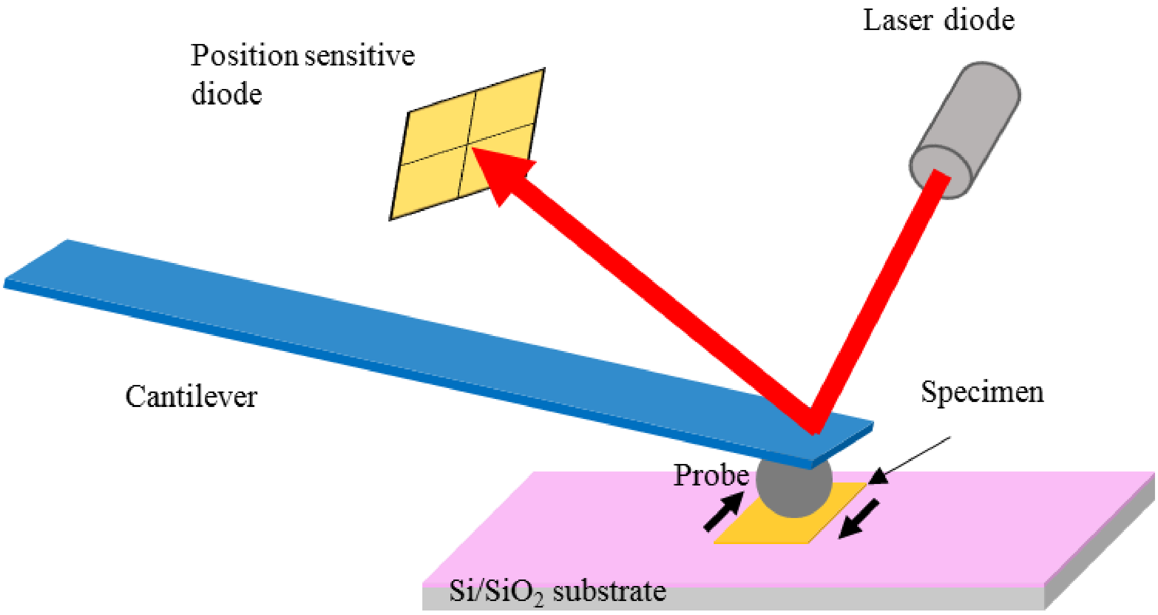

Figure 3. Schematic illustration of the reciprocating scratch test of single layer h-BN, MoS_2, and graphene specimens using silica AFM colloidal probe.

For quantitative assessment of normal and lateral forces, force calibrations were performed in both normal [32] and lateral [33,34] directions, prior to the experiments. The contact pressure between the colloidal probe and specimens is defined as the following equation

$$P = \frac{3F_n}{2\pi a^2} \tag{1}$$

where P is the contact pressure, F_n is the normal force and a is the contact radius which can be calculated from Derjaguin-Muller-Toporov (DMT) model [35] as described below

$$a^3 = \frac{R(F_n + F_{ad})}{K} \tag{2}$$

In equation (2), R is the radius of the colloidal probe, F_{ad} is adhesion force between the colloidal probe and specimen and K is reduced Young's modulus between colloidal probe and specimen. R can be determined based on SEM and confocal microscope images. The value of F_{ad} in equation (2) is determined by pull-off force from the force-distance curves. And the reduced Young's modulus (K) between colloidal probe and specimen is defined as the following equation

$$K = \left[\frac{3}{4}\left(\frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2}\right)\right]^{-1} \tag{3}$$

where E_1, E_2 and v_1, v_2 are Young's modulus and Poisson's ratio of the silica probe and specimens, respectively.

It is noted that to minimize the effect of AFM drift, AFM was set up and kept dummy scans with the same conditions as the real test except the normal force within few hours prior to the reciprocating scratch test. And the colloidal probe had been slid against SiO_2 substrate in few hours prior to the real test. The reciprocating scratch test was conducted right after these steps for single layer h-BN, MoS_2, and graphene specimens, respectively.

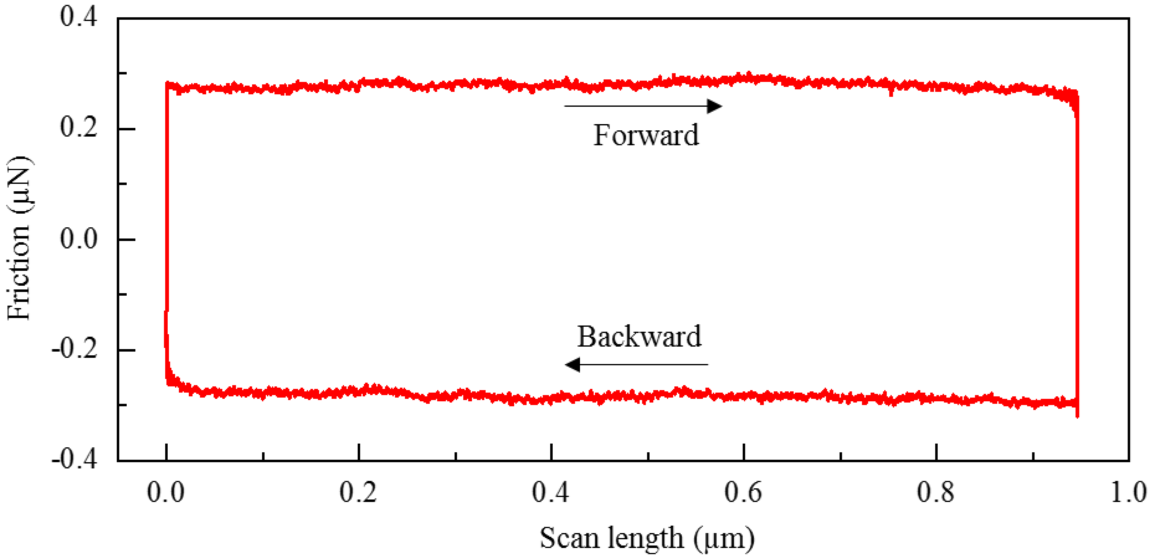

Figure 4. An example of friction loops between colloidal probe and graphene specimen.

Fig. 4 shows an example of a friction loop between the colloidal probe and single layer graphene specimen in reciprocating scratch test. In this experiment, depending on the normal force, the contact pressure is defined from 0.30 to 0.74 GPa corresponding to the contact radius range from 120 to 260 nm defined by DMT model. The friction was monitored during the test to observe the failure of the specimens. And the test was stopped as a significant increase in friction was observed. The details of the results will be discussed in the next section.

2.3 Characterization of specimens after reciprocating scratch test

AFM intermittent contact mode imaging and AFM contact mode imaging were performed after reciprocating scratch test to characterize the topographic and friction force microscopy (FFM) images of specimens after the test. The topographic image was characterized by AFM intermittent contact mode imaging of which the procedure and conditions are the same as those in specimen preparation section. In AFM contact mode imaging, a sharp silicon tip (tip radius of 8 ± 2 nm) with a nominal compliant cantilever of 0.2 N/m (PPP-LFMR, Nanosensors) was used. For quantitative normal force, the AFM cantilever was calibrated using thermal noise method [32] before AFM contact mode imaging. A minimum normal force ~ 1 nN was then applied to the tip when scanning the specimens to minimize the damage of the specimens and the tip during the AFM contact mode imaging. After the lateral force scanning, the tip was calibrated in lateral direction using improved wedge method [36] to determine the lateral force (friction force) with respect to the normal force. All experiments were carried out at ambient conditions with relative temperature of 23 ± 3 ^{o}C and relative humidity of 40 ± 5 %.

Raman spectral imaging were then used to obtain the peak intensity images and characteristic peaks of single layer h-BN, MoS_2, and graphene specimens after reciprocating scratch test. The peak intensities, peak frequencies (peak shift), and the distance between peaks of the wear tracks were carefully compared to those of as-exfoliated areas.

3. SURFACE DAMAGE CHARACTERISTICS OF SINGLE LAYER h-BN, MOS$_2$, AND GRAPHENE

3.1 Initial state of specimens

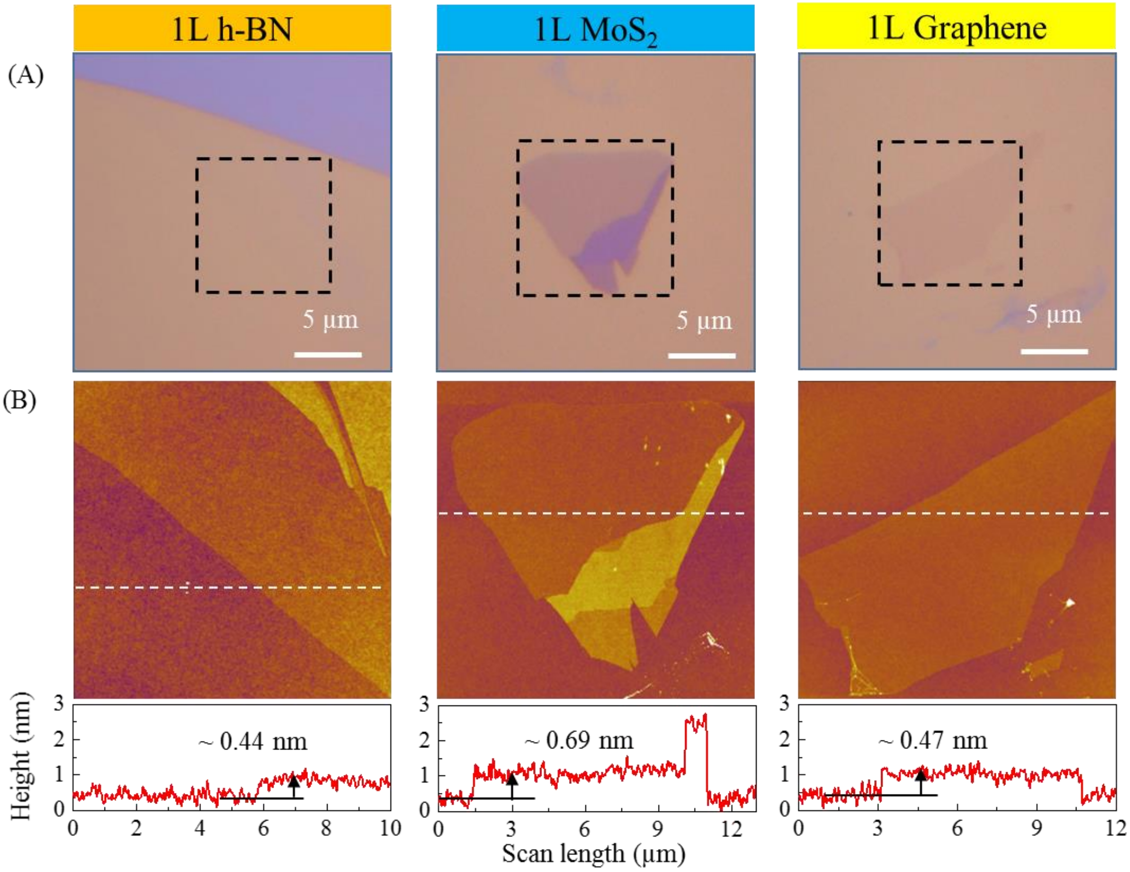

Figure 5. (A) Confocal microscope images of (from left to right) 1L h-BN, MoS$_2$, and graphene on SiO$_2$/Si substrate, respectively. (B) Topographic images of the areas in the black-dash square in (A). In (B), the white dashed lines indicate the locations of the cross-sectional profiles.

Fig. 5 (A) shows the confocal microscope images of single layer h-BN, MoS$_2$, and graphene specimens on the SiO$_2$ substrate, respectively. As shown in this figure, single layer h-BN is nearly transparent and need to well focus to identify its location under a confocal microscope. However, single layer h-BN specimens are usually observed nearby the thicker ones. That is the key to identify location of single layer h-BN specimens. For single layer MoS_2 and graphene, it is easier to determine the locations of these specimens due to the optical contrast differences between the specimens and SiO_2 substrate. AFM topographic images of single layer h-BN, MoS_2, and graphene marked by dashed black squares in Fig. 5 (A) were shown in Fig. 5 (B). The locations of the cross-section profiles are indicated by the white dashed line in the AFM topographic images. It was found that the thicknesses of single layer h-BN, MoS_2, and graphene specimens are ~ 0.44, 0.69, and 0.47 nm, respectively, which generally agree with previous studies [5,37,38]. These thickness values are slightly higher than the theoretical values, which associate with the presence of adsorbents and measurement uncertainties of AFM.

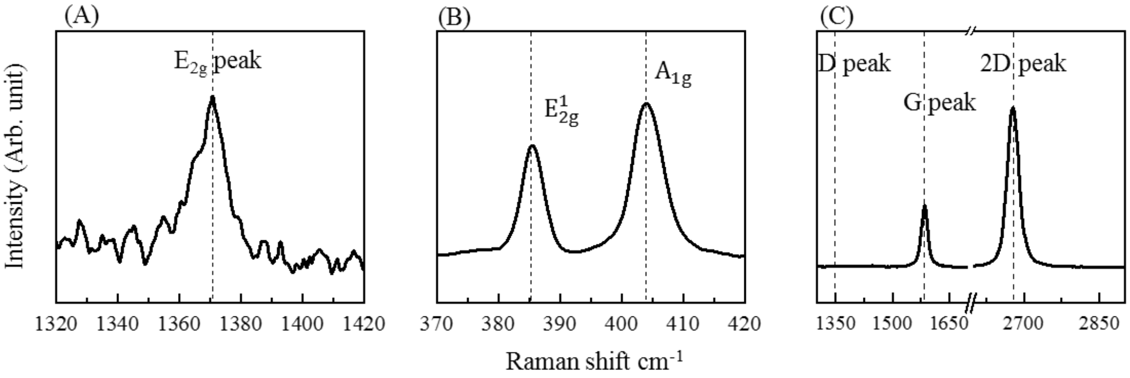

Figure 6. Raman spectra of single layer (A) h-BN, (B) MoS_2, and (C) graphene.

Raman spectra of single layer h-BN, MoS_2, and graphene specimens are shown in Fig. 6. For single layer h-BN, the characteristic peak E_{2g} (located at ~ 1370 cm^{-1}) is a relatively weak peak corresponding to the in-plane vibrations of B-N bonding [39]. In the case of single layer MoS_2 (Fig. 6 (B)), two characteristic peaks were observed at ~ 385.2 (E^1_{2g}) and ~ 403.7 (A_{1g}) cm^{-1} which are corresponding to the in-plane vibrations of Mo-S bonding and out-of-plane vibrations of S atoms. The frequency difference between 2 peaks of MoS_2 specimens is about 18.5 cm^{-1} allowing to determine the peaks of single layer MoS_2 [4,37]. For single layer graphene, two most typical peaks are G peak and 2D peak exhibited at ~ 1580 cm^{-1} and at ~ 2670 cm^{-1} which are represented the in-plane vibrations of the sp^2 carbon atoms and a double resonance Raman process [40-42], respectively. It was found that D peak of ~ 1350 cm^{-1} is not observed in Raman spectra because of defect free of graphene specimens before the reciprocating scratch test [43].

3.2 Surface damage characteristics of single layer h-BN

After characterization of the topographic and thicknesses of single layer h-BN, MoS_2, and graphene specimens, the reciprocating scratch test was conducted using AFM colloidal probe. Fig. 7 (A), (B) shown the topographic and FFM images of single layer h-BN after reciprocating scratch test under various normal forces from 10 to 42 µN, respectively. From the topographic images, at low normal force (10 µN), some wear debris appeared at the end of wear track and no significant changes in topographic image of single layer h-BN (Fig. 7 (A)). The FFM image in Fig. 7 (B) shown no significant change in friction force after 10,000 cycles reciprocating scratch test. Some wear debris which may come from the colloidal probe and small contaminations which may be found in topographic image have not observed in FFM image since they may be moved out of the two ends of wear track during the AFM scanning after the test. However, at higher normal forces, single layer h-BN specimen was easily torn and peeled off from the substrate after few thousand cycles test. A significant decrease in height profiles (Fig. 7(A)), which agrees with a drastic increase in FFM profiles (Fig. 7 (B)), indicates that the specimen has been completely failed. The substrate is clearly observed in both topographic and FFM images. In FFM images, the darker areas, where higher friction force are exhibited, indicate that single layer h-BN specimen has completely failed and the substrate was exposed.

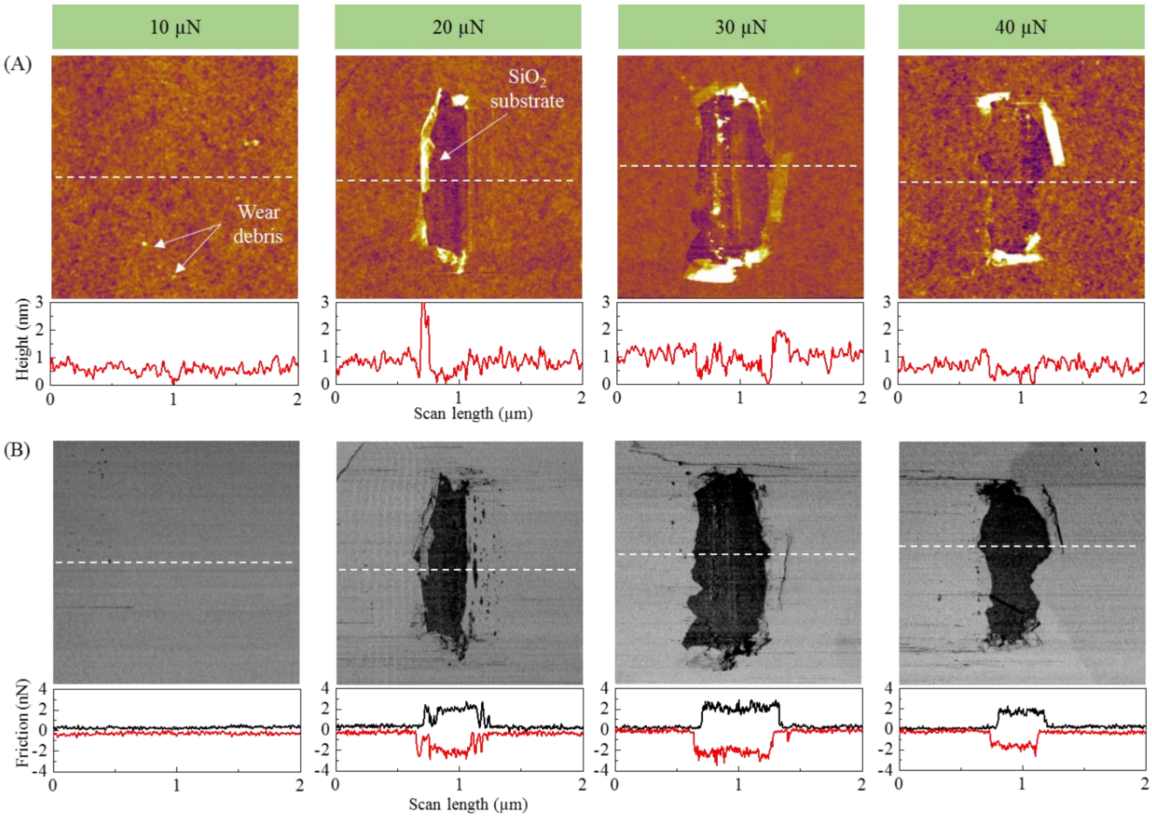

Figure 7. Effect of normal force on surface damage characteristics of single layer h-BN. (A) Topographic and (B) FFM images of 1L h-BN after reciprocating scratch test with the normal force is 10, 20, 30, and 42 µN, respectively.

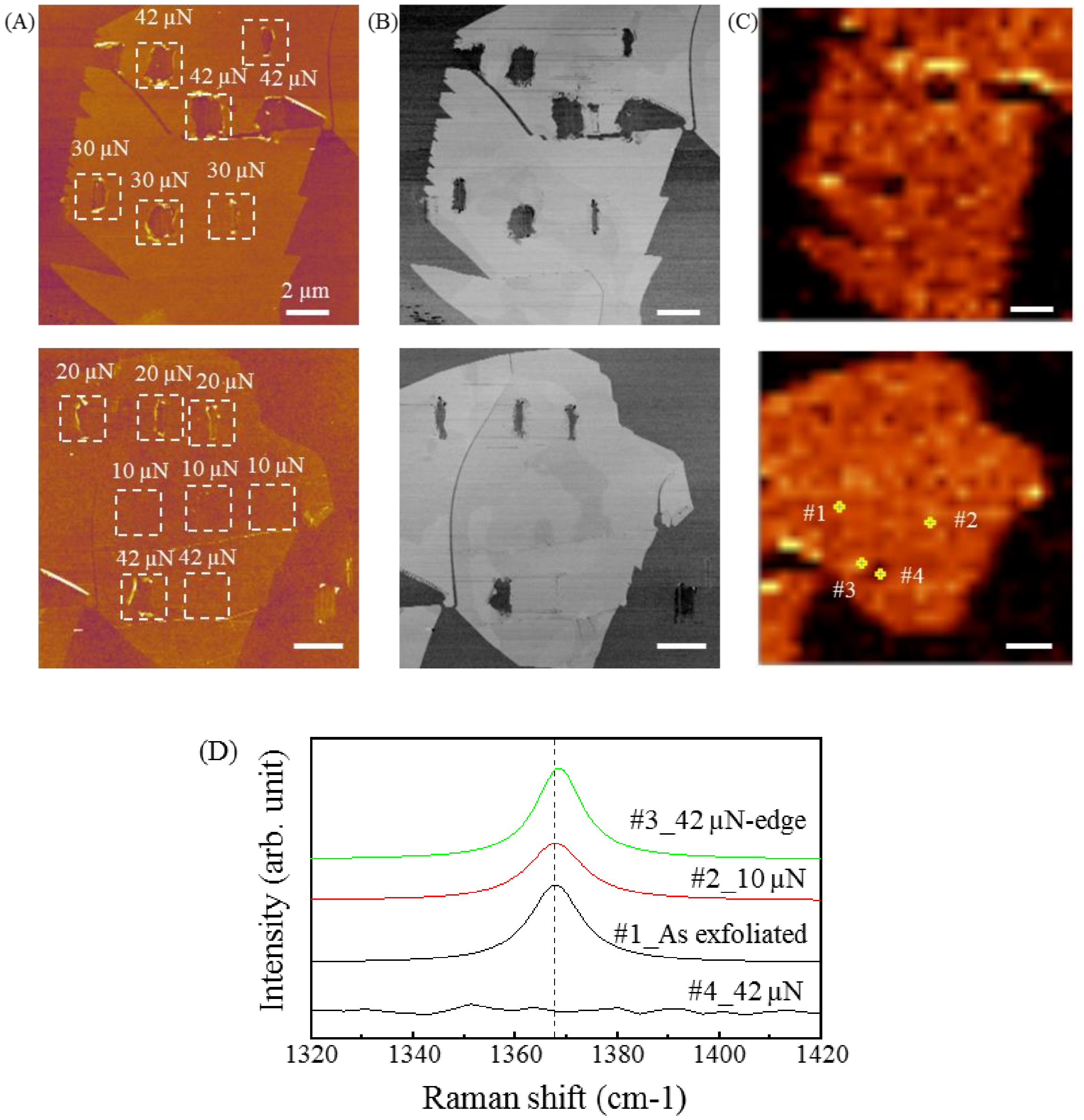

Figure 8. (A) Topographic, (B) FFM, and (C) Raman intensity images of single layer h-BN after reciprocating scratch test at different normal forces. (D) is the graph of Raman spectra of single layer h-BN collected at 4 locations marked from #1 to #4 in (C). All scale bars are 2 µm.

Topographic (A), FFM (B), and Raman intensity images (C) of single layer h-BN after reciprocating scratch test at different normal forces were shown in Fig. 8. Each value of normal force was tested at three different locations to investigate the reproducibility of the experiment. Raman spectra inside the wear track of 10 µN in

Fig. 8 (D) shown no shift of E_{2g} peak when compared to as exfoliated one (spectrum #2 versus spectrum #1 in Fig. 8 (D)). It agrees with AFM results which indicate that specimens have not completely failed yet. At the edges where the specimen was wrinkled and folded, the intensity of E_{2g} peak was significant increases and its frequency increased (blue-shifted) as shown in spectrum #3. The dark regions of wear track, where single layer h-BN was peeled off from the substrate exhibited no intensity of E_{2g} peak (spectra #4 in Fig. 8 (D) where the spectrum was collected inside the wear track of 42 µN normal force).

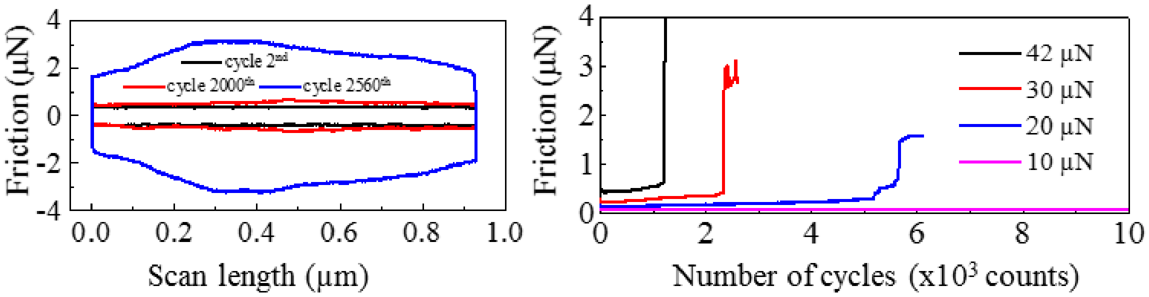

Figure 9. Example of friction loops and variation of friction forces during the reciprocating scratch test of single layer h-BN.

An example of friction loops and the variation friction force are shown in Fig. 9. In this experiment, the number cycles of reciprocating scratch test are defined to 10,000 or to the failure of the specimen. As shown in Fig. 9, a significant increase in friction force is a sign of the failure of the specimen since high friction indicates that the friction between the probe and the SiO_2 substrate was collected. At 10 µN, friction was not significantly changed after 10,000 cycles. However, at higher normal force, h-BN film was easily torn and failed after few thousand cycles test. As the normal force increases, the failure of the film occurred earlier. For instance, single layer h-BN has been completely failed under the normal force of 20, 30, and 42 µN after ~ 5600, 2400 and 1200 cycles, respectively. As shown in Fig. 9, before failure of the sample, the friction force was kept at a small value under 0.5 µN and a significant increase in friction force is a sign of the failure of the specimens. The friction loops in Fig. 9 (A) also indicates this phenomenon. When failed, the specimens were torn and folded to both edges and both ends of wear track. These results help to understand that single layer h-BN can be durable at a contact pressure of ~ 0.3 GPa after 10,000 reciprocating scratch tests. However, as the contact pressure increase to ~ 0.36 GPa, single layer h-BN easily damaged after a few thousand cycles test and the thin film was completely torn and peeled off to expose the SiO_2 substrate as shown in Fig. 7.

3.3 Surface damage characteristics of single layer MoS_2

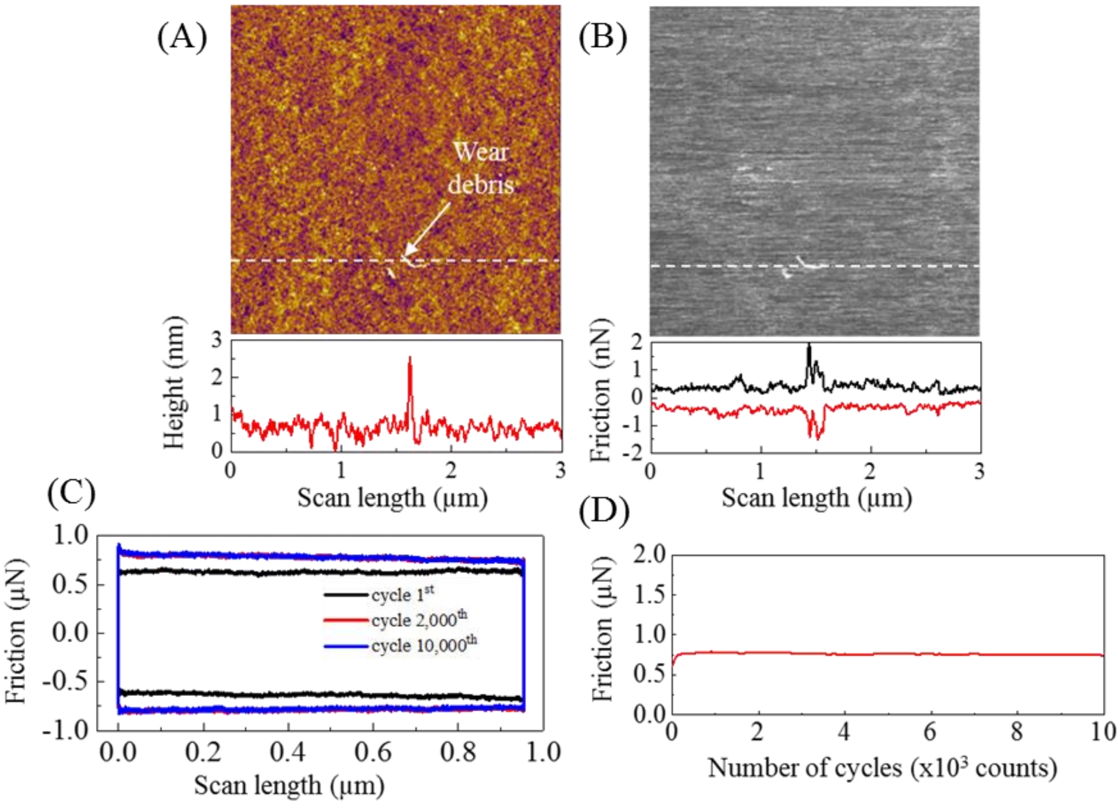

Figure 10. (A) Topographic and (B) FFM images of single layer MoS_2 after 10,000 cycles reciprocating scratch test. (C) Friction loops are taken at different number of cycles. (D) The variation of friction forces during reciprocating scratch test under normal force of 42 µN.

Fig. 10 shows the results of single layer MoS_2 after 10,000 cycles reciprocating scratch test under 42 µN (~ 0.63 GPa). As discussed in results of single layer h-BN specimens under a normal force of 10 µN, after 10,000 cycles under 42 µN normal force some wear debris which may be SiO_2 particles detached from the sliding of silica colloidal probe during the reciprocating scratch test and some small contaminations on the surface of specimens were observed at the end of wear track as shown in Fig. 10 (A), (B)). These made the height and friction at end of wear track significantly increased although MoS_2 specimen was not failed after 10,000 cycles reciprocating scratch test. Fig. 10 (C), (D) shown the friction loops and variation of friction force during the test. The friction loops (Fig. 10 (C)) and variation of friction force (Fig. 10 (D)) shown that friction was not changed much and the value of friction is kept at ~ 0.73 μN during the reciprocating scratch test.

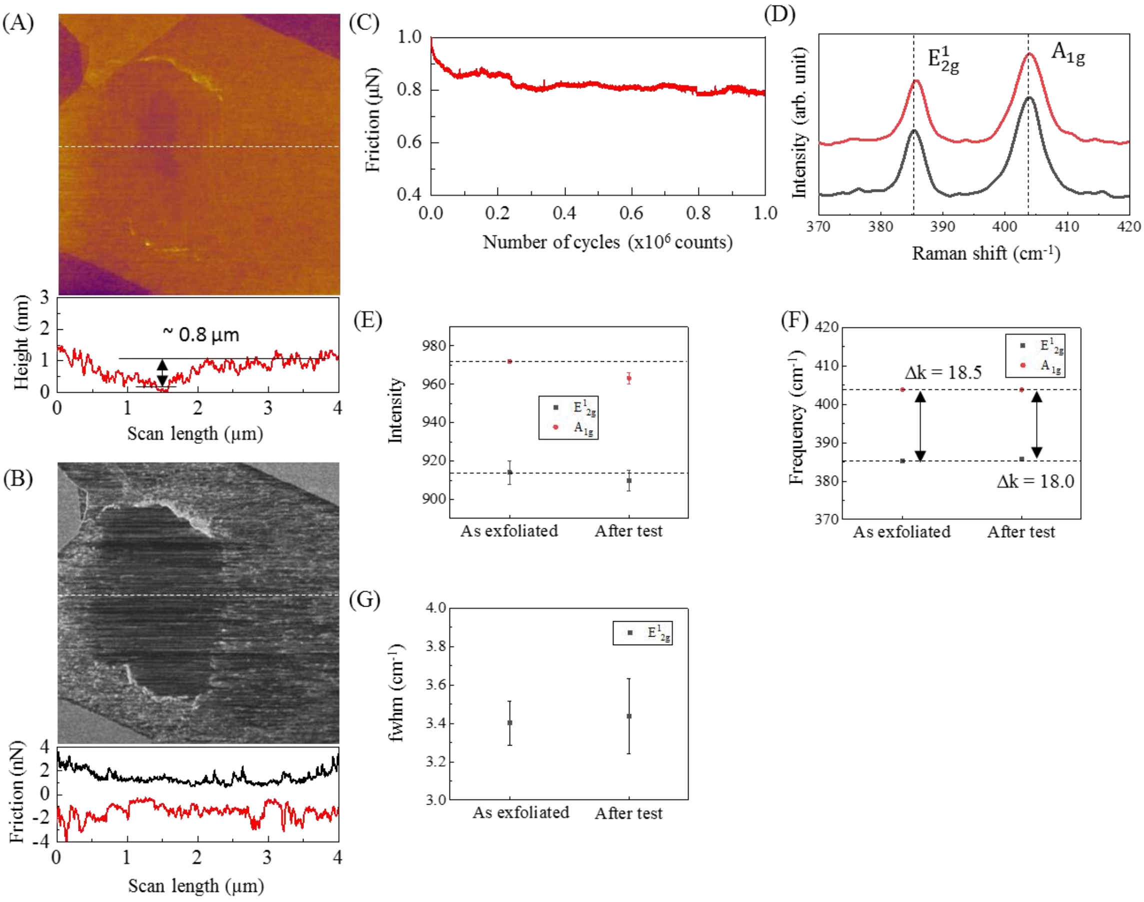

Figure 11. (A) Topographic and (B) FFM images of single layer MoS$_2$ after 1 million cycles reciprocating scratch test. (C) Variation of friction force during reciprocating scratch test. (D) Raman spectra of E^1_{2g} and A_{1g} peaks. (E) intensities, (F) frequencies, and (G) fwhm of E^1_{2g} peak at as exfoliated and at wear track of single layer MoS$_2$. In (A) and (B) the white dashed lines indicate the locations of the cross-sectional profiles.

To further investigate the surface damage characteristics of single layer MoS$_2$, an extend experiment has conducted. The normal force of 70 μN (~ 0.74 GPa) was used in reciprocating scratch test of single layer MoS$_2$ during 1 million cycles. Fig.

11 (A), (B), show the topographic and FFM images of single layer MoS_2 after reciprocating scratch test. The topographic image of single layer MoS_2 after test shows that some wear debris which may be SiO_2 particles detached from the sliding of colloidal probe during the reciprocating scratch test and some small contaminations on the surface of specimens appeared at two ends of wear track as observed in the previous experiment. From height profile in topographic image (Fig. 11 (A)), the height of single layer MoS_2 at wear track after test was observed to be decreased ~ 0.8 nm compared to as exfoliated MoS_2 outside the wear track. However, the friction at wear track is slightly decreased after test (Fig. 11 (B)) since the specimen has been smoother due to the moving of wear debris and some contaminations to both ends of wear track. Wear debris and contaminations were observed at two ends of the wear track where the friction force was found higher compared to as exfoliated areas. This agreed with the increase in height at the two ends of wear track in topographic images as shown in Fig. 11 (A). Fig. 11 (C) shows the variation of friction during the reciprocating scratch test. At early 2.5×10^5 cycles reciprocating scratch test, the friction is slightly high then stabilize at ~ 0.8 µN and maintained around this value to the end of the test. The reason why friction is high at the early time may be because of some contaminations on the surface and these particles could be lead to high friction at cycles of the beginning of the test. After contaminations brought into the two ends, the friction reached at a stable value and did not show significant change until 1 million cycles.

Raman spectra in Fig. 11 (D) clearly shows that the Raman characteristic peak A_{1g} is not shifted. In contrast, E_{2g}^{1} peak shown a slight blue shift after reciprocating scratch test. The peak intensity has a downward trend for both peaks. In details, the peak intensities were reduced from ~ 972 and ~ 914 down to ~ 963 and ~ 910 cm^{-1} for the E_{2g}^1 and A_{1g}, respectively as shown in Fig. 11 (E). The peak frequency difference between E_{2g}^1 and A_{1g} slightly decreased from 18.5 down to 18.0 cm^{-1} (Fig. 11 (F)) and the E_{2g}^1 full-width at half maximum (Fig. 11 (G)) shown no significant change. Some slight changes in Raman spectra of single layer MoS_2 indicates that the compressive strain is relatively low after test [17] and the specimen was not completely failed under a relatively high contact pressure (~ 0.74 GPa) after 1 million cycles of reciprocating scratch test.

3.4 Surface damage characteristics of single layer graphene

Fig. 12 shows the results of single layer graphene after 10,000 cycles reciprocating scratch test under 42 µN (~ 0.51 GPa). As discussed in the test of h-BN specimens at low normal force and the test of single layer MoS_2, the wear debris has observed on topographic image (Fig. 12 (A)). No significant change in friction was observed (Fig. 12 (B)). It means that graphene specimen was not failed under 42 µN after 10,000 cycles reciprocating scratch test. A plastic deformation of SiO_2 substrate of ~ 0.3 nm was observed in topographic image in Fig. 12 (A). Fig. 12 (C), (D) show the friction loops and variation of friction during the test. The friction loops (Fig. 12 (C)) and variation of friction forces (Fig. 12 (D)) confirmed that friction was not changed much and the value of friction is kept at ~ 0.49 µN after 10,000 cycles reciprocating scratch test.

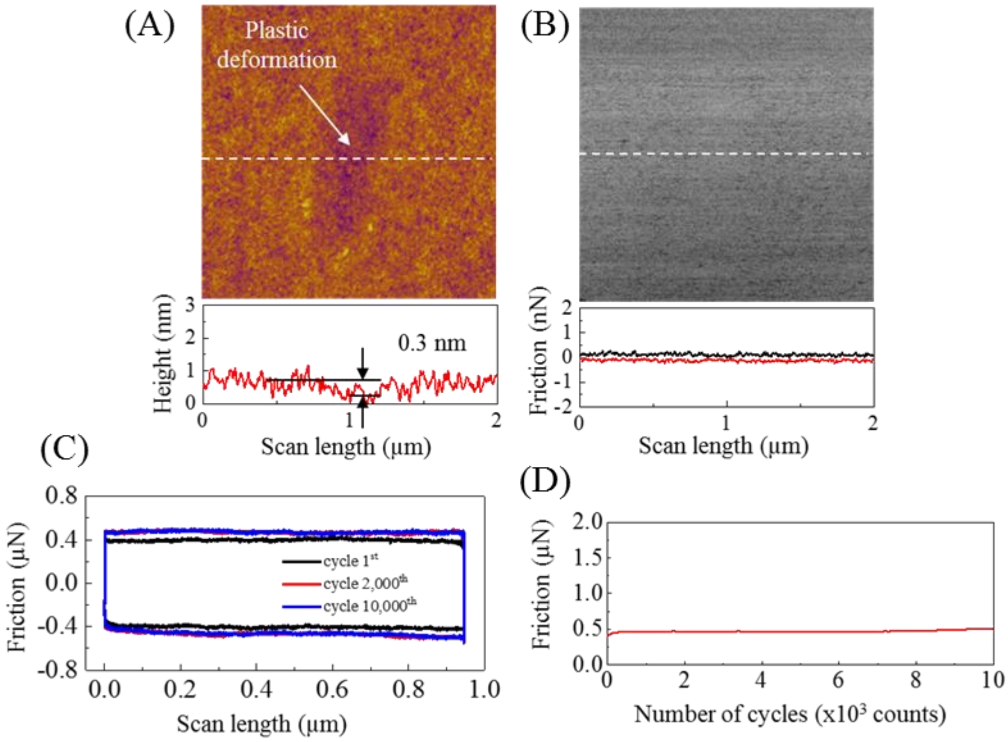

Figure 12. (A) Topographic and (B) FFM images of single layer graphene after 10,000 reciprocating scratch cycles test. Friction loops (C) are taken at different number of cycles. The variation of friction forces (D) during reciprocating scratch test under normal force of 42 μN.

An extend experiment with a higher normal force of 70 μN (~ 0.6 GPa) was conducted during 1 million cycles reciprocating scratch test. Fig 13 shows AFM and Raman results of single layer graphene after 1 million cycles test. From topographic image in Fig. 13 (A), a significant decrease of ~ 0.8 nm was observed in height profile of single layer graphene. This may be the plastic deformation of SiO_2 substrate since no sign of failure of specimen observed on FFM image and the variation of friction force during the test. Wear debris was also observed at two ends as in case of single layer MoS_2 and single layer h-BN at 10 μN normal force. As discussed in those sections, the wear debris may come from SiO_2 particles detached from the sliding of silica colloidal probe during the reciprocating scratch test. Wear debris was then brought to both ends of the wear track due to the reciprocating sliding of the colloidal probe against specimen. Although a significant decrease in height at the wear track, the friction of single layer graphene is relatively similar to as exfoliated areas as observed in Fig. 13 (B) and (C).

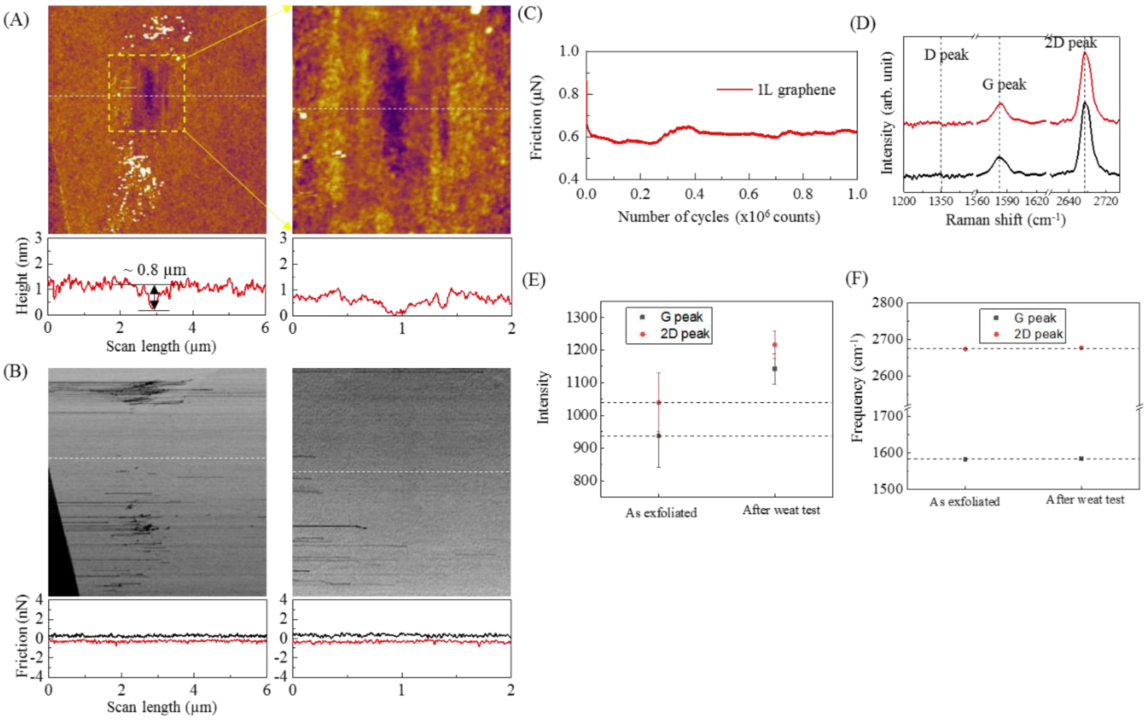

Figure 13. (A) Topographic and (B) FFM images of single layer graphene after 1 million cycles reciprocating scratch test. (C) Variation of friction forces and friction coefficients during reciprocating scratch test. (D) Raman spectra of D, G, and 2D peaks. (E) intensities and (F) frequencies at as exfoliated and at wear track of single-layer graphene. In (A) and (B), the white dashed lines indicate the locations of the cross-sectional profiles.

The value of friction force after ~ 5000 cycles is ~ 0.6 μN and slightly fluctuate to the end of the test. Raman spectra in Fig. 13 (D) shows that there is no shift of 2D peak at wear track after the test. However, a slight shift of about 2 cm^{-1} to the right (blue shift) was observed on G peak. In addition, the intensities of these two peaks have been increased after 1 million cycles reciprocating scratch test. In details, the G peak has shifted ~ 2 cm^{-1} from 1582 to 1584 cm^{-1}. And the difference in intensities between G peak and 2D peak was decreased as observed in Fig. 13 (E) which may cause by in-plane compressive strain of single layer graphene [17]. It was found that after reciprocating scratch test, D peak was not observed in Raman spectra of single layer graphene in Fig. 13 (D). It means that after one million cycles test under a contact pressure of 0.6 GPa, the defect of single layer graphene has not clearly observed and single layer graphene has not completely failed yet.

3.5 Comparison of friction force between SiO_2 substrate and single layer graphene

To implement single layer h-BN, MoS_2, and graphene as protective coating layer with low friction and high wear resistance, an additional reciprocating scratch test between the colloidal probe and SiO_2 substrate has been employed to prove the low friction characteristics of single layer h-BN, MoS_2, and graphene. Fig. 14 shows the topographic and FFM images of SiO_2 substrate and 1L graphene after 1,000 and 10,000 cycles test, respectively. It is shown that a wear track on SiO_2 substrate is observed on topographic due to the slight increase in height profile. Although the contact radius in the test of SiO_2 is ~ 200 nm, the width of the wear track was observed ~ 1 μm because of the effect of AFM drift during the test. The height at wear track slightly increases which may come from the wear debris when colloidal probe (amorphous structure of SiO_2) sliding on SiO_2 substrate. However, in the case of single layer graphene, a slight decrease in height at wear track is observed and there is no significant change in friction force after the test at the same normal force of 42 µN, even the number of cycles is 10 times larger than that on SiO_2 substrate. The variation in friction force and friction coefficient during the wear test were shown in Fig. 14 (C). The friction force between single layer graphene specimen and the colloidal probe is ~ 30 times lower than that between SiO_2 substrate and colloidal probe. Thus, friction coefficient between the colloidal probe and graphene specimen (~ 0.008) is much lower than that between the colloidal probe and SiO_2 substrate. In MEMS and NEMS, where the distance between parts are extremely small, wear debris and friction may be the critical concerns. Therefore, single layer MoS_2 and single layer graphene may be promising candidates for protective coating layers and solid lubricants for micro- and nano-devices due to the high wear resistance and low friction characteristics.

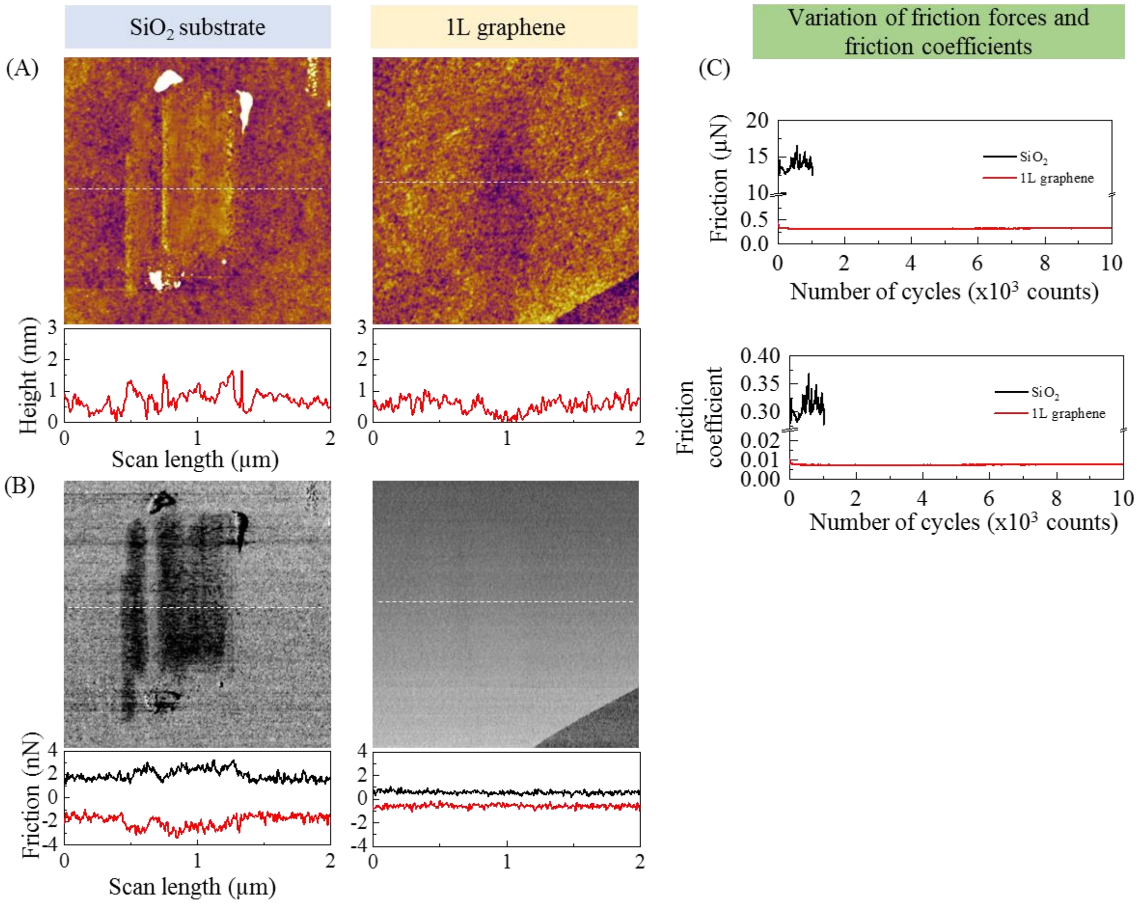

Figure 14. (A) Topographic, (B) FFM images of SiO_2 substrate and single layer graphene after 1,000 and 10,000 cycles reciprocating scratch test, respectively. (C) Variation of friction force and friction coefficient during reciprocating scratch test. In (A) and (B) the white dashed lines indicate the locations of the cross-sectional profiles.

To characterize the effect of tip wear on surface damage characteristics of single layer h-BN, MoS_2, and graphene, AFM topographic image of the colloidal probe at contact area after reciprocating scratch test was observed and compared to that before reciprocating scratch test. As shown in Fig. 15, the topographic along with height profile of colloidal probe at contact area after test shown no significant change. The surface of colloidal probe (Fig. 15, 3D images) is slightly smoother after test which could be the results of some wear debris detached and moved to the two ends of wear track as observed on the topographic image of single layer h-BN at 10 μN normal force, on the topographic image of single layer MoS_2 and single layer graphene specimens.

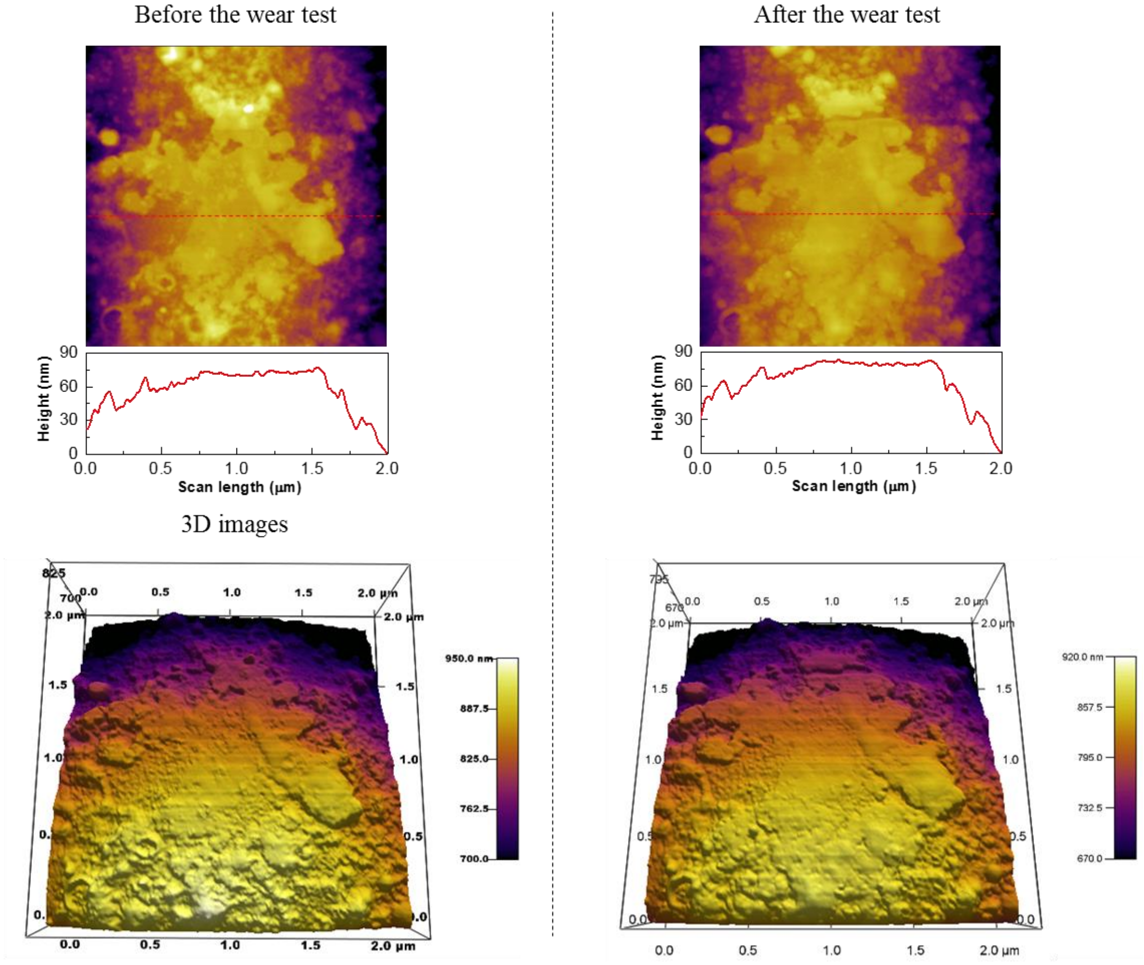

Figure 15. Topographic and 3D images of AFM colloidal probe before and after reciprocating scratch test.

In general, the results of reciprocating scratch test of single layer h-BN, MoS_2, and graphene shown that single layer h-BN was failed at the normal force of 20 μN or higher. The low mechanical strength and weak adhesive strength to the substrate of single layer h-BN [17] could responsible for premature failure of single layer h-BN. Single layer MoS_2 and single layer graphene performed higher wear resistance than single layer h-BN. These layered materials have even not completely failed at the normal force of 70 μN after 1 million cycles reciprocating scratch test. And the plastic deformation of the SiO_2/Si substrate was clearly observed. These findings may helpful for the applications of these materials as protective coating layers to improve the tribological properties of the micro- and nano-systems.

4. CONCLUSION AND RECOMMENDATION FOR FUTURE WORKS

4.1 Conclusions

The surface damage characteristics of single layer h-BN, MoS_2, and graphene has been systematically investigated using AFM and Raman spectra. It was found that single layer h-BN is lower wear resistance compared to single layer MoS_2 and single layer graphene. Single layer h-BN was failed at the early time under high contact pressure and the failure of single layer h-BN is proportional to the normal force. However, single layer h-BN performed low friction characteristics before failure as those of single layer MoS_2 and single layer graphene.

Another finding in this work is single layer MoS_2 and single layer graphene have not failed yet under a high contact pressure after one million cycles of reciprocating scratch test. Although a plastic deformation of the SiO_2 substrate was observed after 1 million cycles of reciprocating scratch test under 70 µN normal force. These findings may propose single layer MoS_2 and single layer graphene as protective coating layers and solid lubricants for mico- and nano-devices for long-term operation. Based on single layer MoS_2 and single layer graphene, tribological properties of the micro- and nano-devices may be improved and operational lifetime of the devices may be prolonged.

4.2 Recommendation for future works

Study on the surface damage characteristics of single layer h-BN, MoS_2, and graphene with a higher contact pressure using AFM colloidal probe may helpful to propose single- and few-layer h-BN, MoS_2, and graphene as potential protective coating layers for various application in MEMS and NEMS.

Study on the effect of relative humidity and temperature on surface damage characteristics of single- and few-layer h-BN, MoS_2, and graphene will give a better understanding of surface damage characteristics of atomically thin h-BN, MoS_2, and graphene for the tribological applications in various environments of micro- and nano-devices.

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