Intrinsic structure and friction properties of graphene and graphene oxide nanosheets studied by scanning probe microscopy

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Abstract. In this paper, atomic structure of single-layered graphene oxide (GO) and chemically reduced graphene oxide (CRGO) nanosheets was investigated using atomic force microscopy and scanning tunneling microscopy (AFM and STM). Furthermore, friction properties of the graphene and GO nanosheets were studied by frictional force microscopy (FFM). STM imaging provided direct evidence and the morphology was influenced by oxygen-containing groups and defects. The atomic scale structural disorder in a hexagonal two-dimensional network of carbon atoms changes the surface condition, which also caused the frictional property variations of the samples.

Keywords. Graphene oxide; graphene; AFM; STM; FFM; frictional property.

1. Introduction

Graphene, a single layer of graphite, has attracted great interest in recent years because of the unique physical, chemical and mechanical properties arising from its strictly 2-D structure. The unique properties hold great promise for potential applications in many technological fields such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors and hydrogen storage (Allen *et al* 2010; Dreyer *et al* 2010; Loh *et al* 2010). Since Geim and coworkers at Manchester University first isolated single-layer graphene from bulk graphite in small amounts by micromechanical cleavage, many methods have been developed for preparing graphene including chemical vapour deposition (CVD), epitaxial growth and chemical reduction of exfoliated graphite oxide (Shiroyama 2001; Pan *et al* 2009; Park and Ruoff 2009). Of these routes, chemical method is considered to be an efficient approach to producing processable graphene sheets in bulk quantity at a relatively low cost.

In general, graphene oxide has been mainly prepared by the modified Hummer's methods. These methods involve oxidation of graphite powder in the presence of strong acids and oxidants. The sp^2 -bonded carbon network in graphite is readily destroyed and some parts of the C atoms are bonded to hydroxyl groups and epoxide groups and edges of the layers are attached to carboxylic or carbonyl groups. GO is strongly hydrophilic and is easily exfoliated in water because, large amounts of oxygen containing groups existed on the basal or edge plane. Reduction of the graphene oxide using reductants such as hydrazine, dimethylhydrazine and $NaBH_4$ caused the agglomeration and precipitation of CRGO (Stankovich *et al* 2006, 2007; Muszynski *et al* 2008; Wang *et al* 2008). Most studies suggested that the graphene

stemmed from reduction of graphene oxide which contained a significant amount of oxygen groups and a large number of defects (Gass *et al* 2008; Allen *et al* 2010). Because, the electronic, thermal and mechanical properties of graphene and GO are exceptionally sensitive to the atomic structure and it is critically important to get information about the functional groups and defects of graphene prepared by chemical methods.

Scanning probe microscopy is one of the most powerful modern research techniques that allows study of morphological features and local properties of the surface with high spatial resolution. In this paper, we used AFM and STM to probe the local atomic structure and morphology of single layer GO and graphene nanosheets under ambient conditions. Microtribological behaviours of single-layer graphene and GO sheets on mica surface were also tested by FFM.

2. Experimental

2.1 Preparation of GO and graphene

Graphite oxide was prepared from natural graphite powder by a modified Hummers method (Ding *et al* 2010). In a typical procedure, 1.5 g graphite powders were first oxidized by reacting them in a mixture of 35 ml concentrated nitric acid and 70 ml concentrated sulfuric acid in an ice bath. And then, 9 g potassium permanganate was added to the container slowly (Notice: the reaction will get out of control if potassium permanganate was added quickly). After reaction at 65 °C for 120 h, 100 ml deionized water was added dropwise to the container carefully. Then the reaction was allowed to go on at 90 °C for 2 h to fully oxidize graphite into graphite oxide. The graphite oxide was washed with dilute hydrochloric acid and deionized water until pH of the washing solution increased to neutral (~ 7). Graphite oxide was dispersed in

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a mixture of deionized water and *N,N'*-dimethylformamide (DMF) and exfoliated through ultrasonication for 1 h. The final GO dispersion was reduced by hydrazine hydrate at 100 °C for 24 h.

2.2 Characterization

Powder X-ray diffraction (XRD) was carried out using a Bruker D8 Advance X-ray diffractometer. AFM measurements for nanometer-scale morphology were taken with a Digital Instruments NS3D from Veeco in tapping mode using silicon tips with a resonance frequency of 125 kHz. STM measurements were performed in the constant current mode with mechanically prepared Pt/Ir tips and *A(E)* scanners. Microtribological behaviours of single-layer graphene and GO sheets on mica surface were also tested by FFM using a silicon RTESP tip. All STM and AFM experiments were carried out under the same test condition.

3. Results and discussion

XRD patterns of the natural graphite, GO and CRGO are recorded in figure 1. Agglomeration is caused easily in the process of preparation of GO and graphene sheets because of their higher surface energy. Compared with pristine graphite, stacking structure is still observed in GO and graphene powders and the layer-to-layer distance can be calculated by Bragg equation. The feature diffraction peak of exfoliated GO appears at 11.0° with increased layer-to-layer distance of 0.80 nm, which was identical with those reported in literature (Wang *et al* 2008). The expanded layer spacing was caused by intercalated hydroxyl, epoxy and carboxyl groups between layers. After the exfoliated GO is chemically reduced, the diffraction peak of CRGO is similar to that of graphite with significantly reduced intensity.

Figure 1. XRD patterns of natural graphite (black line), GO (red line) and CRGO (blue line) powders. GO and graphene showing expanded basal spacing.

This implies that most of the functional groups are removed and it should be noted that graphene sheets tend to form irreversible agglomerates or even re-stack to form graphite through strong π - π stacking and Van der Waals interaction (Li and Kaner 2008).

For AFM and STM investigations, unreduced GO and CRGO dispersions were drop-cast onto freshly cleaved, atomically flat and highly oriented pyrolytic graphite (HOPG) substrates (ZYH grade, from SPI corporation) and then allowed to dry in air at room temperature. AFM was carried out in tapping mode with a super sharp tip to obtain high spatial resolution images under ambient conditions (relative humidity, ~45% and temperature, ~25 °C). As shown in figure 2, exfoliated GO are flat sheets with an average thickness of about 1.5 nm. Thickness of CRGO sheets is about 1.0 nm with lateral dimension in the range of hundred nanometers to several microns. Roughness of GO and CRGO (in $1 \times 1 \mu\text{m}$ region) are 0.367 and 0.153 nm,

Figure 2. Tapping mode AFM images of exfoliated GO (a) and CRGO (b). Samples were prepared by drop-casting corresponding dilute dispersions onto mica sheets.

Figure 3. STM images of HOPG (a), exfoliated GO (b) and CRGO (c). Tunneling parameters: $I = 0.5$ nA, $V = 50$ mV (a); $I = 0.3$ nA, $V = 120$ mV (b) and $I = 0.2$ A, $V = 80$ mV (c). Raw STM data in left show lattice image of samples and 2D-FFT measured lattice periodicity for samples shown in right.

respectively. Rough morphology of GO sheets is ascribed to the structural disorder induced by oxidation.

To obtain further information on the local atomic structure and to assess the quality and continuity of GO and CRGO, STM is used to image the samples which are shown in figure 3. From figure 3(a), we can see that commonly reported triangular lattice is with a bias voltage of 50 mV (sample positive) and a tunneling current of 0.5 nA. Both triangular and honeycomb structures are simultaneously observed with the scan area decreased down to 1.5 nm (as insert). The peak-to-peak distance between spots of ~ 0.24 nm was measured, which is very close to the theoretical value of ~ 0.25 nm (Affoune *et al* 2001). 2-D fast Fourier transform (FFT) plot is extremely useful in removing electrical and acoustic noise from images and may also be used to isolate certain surface features (Mao *et al* 2004). The corresponding FFT of STM image from figure 3(a) shows a hexagonal pattern and allows a quantification of the periodicity to 0.246 nm. Similar constant height studies were performed on an oxidized graphene sheet as shown in figure 3(b). The results reveal that parts of oxidized graphene surface have a weak triangular lattice similar to HOPG (120 mV, 0.3 nA). As shown in figure 3(b), it is interesting that there are many disorganized ‘big’ atoms around the orderly arranged C atoms. Apparent ‘big’ atoms may be O atoms or hydroxyl groups bonded to the top and bottom of a graphene sheet to form GO. Contrary to previous reports (Pandey *et al* 2008), we have not directly observed rectangular array of O atoms that are bound to the graphene sheet, but rectangular lattice can also be seen in FFT image. It indicated the periodic structure of graphite which is destroyed during the oxidation. For CRGO, a periodic structure similar to graphite is caught under 60 mV and 0.3 nA. The corresponding FFT image provides evidences to show reconstruction of honeycomb structure from GO to CRGO.

Frictional properties of the samples on a mica surface were measured using FFM mode of an ambient AFM system. The tests were performed in $1 \times 1 \mu\text{m}$ region with a scanning rate of 1 Hz. The normal force (F_Z), frictional force (F_L) and friction coefficient (μ) could be calculated by the following formulas (Schwarz *et al* 1996):

$$F_Z = \frac{Et^3w}{4L^3m} \Delta V_V, \quad (1)$$

$$F_L = \frac{Gwt^3}{4L^2hm} \Delta V_L, \quad (2)$$

$$\mu = \frac{F_L}{F_Z} = \frac{\frac{Gwt^3}{4L^2hm} \Delta V_L}{\frac{Et^3w}{4L^3m} \Delta V_V} = \left(\frac{GL}{Eh} \right) \left(\frac{\Delta V_L}{\Delta V_V} \right), \quad (3)$$

where w , L , t , m , E and G denote the width, length, thickness, sensitivity, Young’s modulus and torsion modulus of the cantilever respectively, h the height of the tip. ΔV_L and ΔV_V the displacement–voltage of the cantilever caused by torsion and bending respectively. Data of

Figure 4. Normal vs average frictional force measured using same AFM tip averaged over repeated measurements on HOPG, GO and graphene.

Figure 5. Effect of scanning rates on frictional forces.

the frictional force and the normal force under different set-point were shown in figure 4. Setpoint voltage varied from 0 to 1.0 V, which indicated the normal force was in the range of 0–200 nN. As shown in the figure, frictional force increased along with the normal force. It is shown that the frictional force is linearly proportional to the normal force. After linear fitting, the friction coefficients of HOPG, graphene and GO were 0.0025, 0.0041 and 0.0370, respectively. Remarkably, the frictional force was not equal to zero when the normal force applied on AFM tip was set to zero, which could be caused by the adhesion force between the tip and surface of samples (Ding *et al* 2011).

As shown in figure 5, the effect of scanning rate on the frictional force was also studied. During the friction, adhesion alternated with slipping between AFM tip and surface of the samples. With the increase of scanning rate, increase of kinetic energy could make it difficult for the complete

formation of a meniscus. It indicated that the frictional force decreased along with the increase of scanning rate. Furthermore, the larger the adhesion force between the tip and the surface is, the more effect it has on the frictional force induced by the scanning rate.

4. Conclusions

The atomic scale structural features of single-layer GO and graphene nanosheets prepared by chemical method were studied by STM. 2D-FFT plots exhibited a reconstruction of honeycomb structure from GO to CRGO. FFM results showed that the frictional force is linearly proportional to the normal force of GO, graphene and HOPG. The friction coefficients of HOPG, graphene and GO were 0.0025, 0.0041 and 0.0370, respectively. For all the three samples, the frictional force decreased along with the increase of scanning rate.

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References

- Affoune A M, Prasad B L V, Sato H, Enoki T, Kaburagi Y and Hishiyama Y 2001 *Chem. Phys. Lett.* **348** 17
- Allen M J, Tung V C and Kaner R B 2010 *Chem. Rev.* **110** 132
- Ding Y, Jiang Y, Xu F, Yin J, Ren H, Zhuo Q, Long Z and Zhang P 2010 *Electrochem. Commun.* **12** 10
- Ding Y, Zhang P, Ren H, Zhuo Q, Yang Z, Jiang X and Jiang Y 2011 *Appl. Surf. Sci.* **258** 1077
- Dreyer D R, Park S, Bielawski C W and Ruoff R S 2010 *Chem. Soc. Rev.* **39** 228
- Gass M H, Bangert U, Bleloch A L, Wang P, Nair R R and Geim A K 2008 *Nature Nanotechnol.* **3** 676
- Li D and Kaner R B 2008 *Science* **320** 1170
- Loh K P, Bao Q, Ang P K and Yang J 2010 *J. Mater. Chem.* **20** 2277
- Mao G, Dong W, Kurth D G and Möhwald H 2004 *Nano Lett.* **4** 249
- Muszynski R, Seger B and Kamat P V 2008 *J. Phys. Chem. C* **112** 5263
- Pan B Y, Zhang H, Shi D, Sun J, Du S, Liu F and Gao H 2009 *Adv. Mater.* **21** 2777
- Pandey D, Reifengerger R and Piner R 2008 *Surf. Sci.* **602** 1607
- Park S and Ruoff R S 2009 *Nature Nanotechnol.* **4** 217
- Schwarz U D, Koster P and Wiesendanger R 1996 *Rev. Sci. Instrum.* **67** 2560
- Shiroyama H 2001 *J. Mater. Sci. Lett.* **20** 499
- Stankovich S *et al* 2006 *Nature* **442** 282
- Stankovich S *et al* 2007 *Carbon* **45** 1558
- Wang G, Yang J, Park J, Gou X, Wang B, Liu H and Yao J 2008 *J. Phys. Chem. C* **112** 8192