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Surface adhesion properties of graphene and graphene oxide studied by colloid-probe atomic force microscopy

Yan-Huai Ding[a,b,*], Ping Zhang[b], Hu-Ming Ren[b], Qin Zhuo[b], Zhong-Mei Yang[b], Xu Jiang[b], Yong Jiang[b]

[a] *Chemical Process Simulation and Optimization Research Center of Ministry of Education, Xiangtan University, Hunan 411105, China*
[b] *Institute of Rheology Mechanics, Xiangtan University, Hunan, 411105 China*

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ABSTRACT

Surface adhesion properties are important to various applications of graphene-based materials. Atomic force microscopy is powerful to study the adhesion properties of samples by measuring the forces on the colloidal sphere tip as it approaches and retracts from the surface. In this paper we have measured the adhesion force between the colloid probe and the surface of graphene (graphene oxide) nanosheet. The results revealed that the adhesion force on graphene and graphene oxide surface were 66.3 and 170.6 nN, respectively. It was found the adhesion force was mainly determined by the water meniscus, which was related to the surface contact angle of samples.

1. Introduction

People's interests in graphene have been growing rapidly over the past few years since it was experimentally discovered by Geim and co-workers at Manchester University [1–4]. Graphene and its derivatives are expected to be used for various applications in the fields of energy storage, nanoelectronics, nanomachines and composite materials due to the remarkable properties of graphene nanosheets including Young's modules, fracture strength, specific surface area and thermal conductivity [5,6]. Graphene has been prepared by several methods such as chemical vapor deposition, mechanical exfoliation, epitaxial growth and chemical method [6–8]. Among these methods, chemical reduction of graphene oxide (GO) is low-cost and effective in producing single or few layers of graphene [9]. The chemical methods mainly involve the oxidation of graphite into graphite oxide and the reduction of GO into graphene nanosheets [10].

Atomic force microscopy (AFM) in tapping mode is commonly used to measure the thickness of single and few layer graphene on mica surfaces [11]. However, a review of literature showed that the thicknesses of a single layer graphene and GO were estimated to range from 0.5 to 2 nm.

It was difficult to identify individual graphene from GO nanosheet using nanoscale thickness measurements. Force spectroscopy, which measures forces on the AFM probe tip as it approaches and retracts from the surface, offers a new tool to study the surface state of graphene and GO on the micron to nanometer scale.

In this paper we focus on the force spectroscopy of graphene and GO recorded by AFM force mode. The normal force on the cantilever, which is related to the adhesion force, is measured as a function of the reaction time in reduction of GO.

2. Materials and methods

2.1. Preparation of materials

Graphite oxide powders were prepared from natural graphite by a modified Hummers method [9]. Natural graphite powder was first oxidized by reacting with concentrated nitric acid and sulfuric acid (1:2, v/v). The reaction unit was immersed in an ice bath, and potassium chlorate was added to the mixture slowly. After the reaction of 120 h, the obtained graphite oxide was thoroughly washed and filtered by deionized water until pH 7. The GO suspended in a mixture of ethanol and water was exfoliated through ultrasonication for 2 h. The obtained GO dispersion was reduced by hydrazine hydrate at 100 °C for 2, 4, 6 and 10 h. The samples by reduced GO for 10 h were named as RGO.

2.2. Characterization

AFM measurements for morphology and thickness were taken with a Digital Instruments Nanoscope IIIA from Veeco in tapping mode using silicon tips with a resonance frequency of 260 kHz. The

* Corresponding author. Tel.: +86 731 58293861; fax: +86 731 58293240.
E-mail address: yhding@xtu.edu.cn (Y.-H. Ding).

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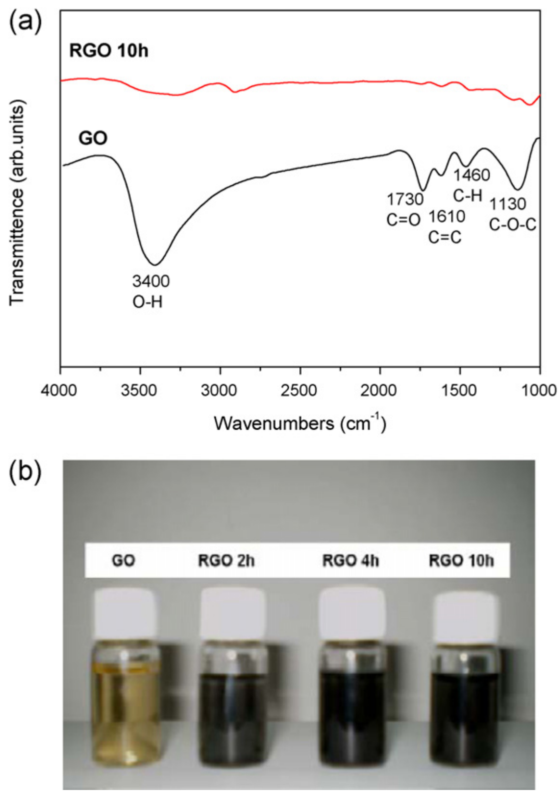

Fig. 1. (a) Comparison of infrared spectra of the GO and RGO powders. The absorption bands located at 3400, 1730 and 1130 cm^{-1} include the signal of hydroxyl, carboxyl and ether groups. (b) The change in color of GO solution reduced by hydrazine hydrate for 2, 4, 6 and 10 h.

force measurements were performed by colloidal probe at 25 °C with humidity of 45%RH. Fourier transform infrared (FTIR) spectrums of the samples were taken on a Perkin–Elmer Spectrum One B. Raman scattering was performed on a Lab Ram-1B Raman spectrometer using a 488 nm laser source.

3. Results and discussions

3.1. FTIR spectrums and photographs of GO and RGO

FTIR spectrums (Fig. 1a) can give a qualitative measure of the deoxygenating reactions of GO. The spectrum of the raw GO showed a rich collection of transmission bands corresponding to carboxylic acid, epoxide groups, and hydroxyl groups, all of which were nearly eliminated after the reduction by hydrazine hydrate for 10 h. The color change of reaction mixture is shown in Fig. 1b. The reaction caused the color of the dispersion to change quickly from pale-yellow to black only in 2 h. It was suggested most of oxygen groups can be eliminated in a short time. After the reduction of 10 h, the sp^2-bonded carbon network of graphite was restored according to the FTIR spectrum.

3.2. AFM characterization of GO and RGO nanosheets

Fig. 2 shows the tapping mode AFM images of highly oriented pyrolytic graphite (HOPG), GO and reduced GO at 10 h. The samples used for AFM studies were prepared by depositing the dispersions on new cleaved mica surfaces and dried under vacuum at 40 °C except for HOPG. The cross-sectional profile of the typical AFM image of the exfoliated GO indicated the average thickness of a single GO sheet was ∼1.5 nm. There were many folds and bumps occurring at the surface of GO nanosheet because of the existence of rich groups such as epoxy and hydroxyl groups. Therefore, GO nanosheet was expected to be thicker than a single layer graphene or a single layer of HOPG. The thickness of an RGO sheet decreased to ∼1 nm after 10 h. The thickness of a single layer on top of HOPG was about 0.6 nm. Thickness of GO and graphene in AFM measurements was several times as much as a pristine graphene (∼0.34 nm), which could be ascribed to absorbing solvent molecules onto the both sides of nanosheets and residual unreduced oxygen groups [4].

3.3. Raman spectra of GO and RGO nanosheets

The Raman spectrum of graphene is characterized by the G mode arising from the first order scattering of the E_{2g} phonon of sp^2 C atoms (∼1575 cm^{-1}) and the D mode arising from a breathing mode of *k*-point photons of A_{1g} symmetry (∼1350 cm^{-1})[12]. D-band and G-band correspond to sp^2 and sp^3 carbon stretching modes and their intensity ratio (I_D/I_G) is a measure of the amount of disorder present in graphene materials. It was clearly seen from Fig. 3 the frequency of the G and D-bands in the RGO was very similar to that observed in the GO. It should be noted that the Raman D/G intensity ratio of RGO was higher than that for the as-made GO, which indicated an increase in the number of smaller graphene domains.

3.4. Surface force curves of GO and RGO

The ability of AFM to create three-dimensional micrographs with resolution down to the nanometer scale has made it an essential tool for imaging surfaces of nanomaterials. Under ambient conditions, a water bridge has been formed between an AFM tip and a surface. This nanoscale bridge exerts a substantial force on the AFM tip. Besides the topographical imaging, AFM can record the force felt by the cantilever as the tip is brought close to-and then pull away. The force plot is an observation of tip-sample interactions which yields information about the sample or tip [13].

The illustration of tip-meniscus-sample system is shown in Fig. 4. The adhesion force *F* between tip and sample surface is determined by capillary force, which is assumed to be the sum of water surface tension and pressure difference on the water meniscus surface. The capillary force *F* can be written as

$$F = \frac{\pi\gamma R^2 \sin^2\varphi\left[\cos(\theta_1+\varphi)+\cos\theta_2\right]}{R(1-\cos\varphi)+d} + 2\pi R\gamma\sin\varphi\sin(\theta_1+\varphi) \tag{1}$$

Here γ is surface tension of water, R is diameter of colloidal sphere, θ_1 and θ_2 are water contact angle of colloidal sphere and sample, respectively. d is distance between colloidal sphere and sample, 2φ is central angle corresponding to water meniscus. The diameter of colloidal sphere is far more than the curvature radius of water meniscus, therefore φ is assumed to be equal to zero. When $\varphi \to 0$, the Eq. (1) can be reduced to

$$F = 2\pi\gamma R(\cos\theta_1 + \cos\theta_2) \tag{2}$$

The calculation of adhesion force includes the following procedures: (1) Sensitivity is expressed as the photodiode voltage versus the distance traveled by the piezo scanner. We can calibrate the sensitivity on a material much stiffer than the cantilever is. (2) Spring constants of the cantilever are determined by the thermal noise method. (3) The adhesion force can be calculated as the following method [13]

$$F = Z \times s \times K \tag{3}$$