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Lateral Size of Graphene Characterized by Atomic Force Microscope

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Abstract. Graphene is a two-dimensional (2D) material possesses unique electronic, magnetic, optical, and mechanical properties that promise to many applications. It has been mass produced and successfully used as composites materials in the form of powder and dispersion. The lateral size and its distribution of graphene sheets are very important to the performance of composites materials. Atomic force microscopy (AFM), scanning electron microscopy (SEM) and optical microscope are normally used to explore the morphology and topological structure of graphene, and further to calculate the lateral size using image processing methods based on the pixels and chromatic aberrations. In this work, lateral size of graphene sheet was calculated based on the topographic height imaging, which is much accurate and convenient and can be used to other 2D materials.

1. Introduction

Atomic force microscopy (AFM) is a tool that invented to image the topography of surfaces [1]. Since its birth in 1986 [2], AFM has evolved into a powerful, multifunctional imaging platform that enable measurement of properties include nanomechanics, nanoelectromechanics, nanoelectrics, nanospectroscopy, and nanoelectrochemistry [3]. Because of its high resolution and its ability to provide a wealth of information with the sample morphology at nanoscale, it has been widely used in many fields including on low-dimensional materials, molecular and cell biology [4, 5]. It can be performed using the three primary AFM imaging operation modes: contact mode, tapping, and non-contact mode [3]. We used a non-resonance intermittent contact mode well-known as PeakForce tapping (PFT) which is based on fast captures and real-time analysis.

The recent discovery of graphene, a single layer of carbon atoms covalently bonded in a honeycomb-like structure, opened a floodgate that result in the discovery and study of other 2D crystals and heterostructures [6, 7]. As 2D materials like graphene become increasingly promising in the areas of composites, energy research, fundamental properties such as average flake size, shape, concentration, and density of defects are among the most significant properties affecting material's

function. The intrinsic properties like thermal conductivity, electrical conductivity, and mechanical performance and of graphene are correlated with flake dimensions [8, 9]. For the ordered dispersion of graphene like nematic liquid crystal (LC) phase graphene oxide, the sizes and the oxidation degrees directly affect formation and behavior of LCs [10, 11]. For the polymer composites based on graphene, smaller flake size decrease the stacking of nanoplatelets due to the highest aspect ratio and specific surface area, larger flake size would result in higher thermal stability to the corresponding composites, increasing the degradation temperature and decreasing the degradation rate [12]. For aluminum composites based on graphene, small sized graphene may improve the fracture toughness, hardness and elastic modulus of the composites due the effect on the crack propagation, larger sized graphene would resulted in grain boundary sliding on the other hand [13]. Efforts have been made to obtain graphene with expected flake size [14, 15].

The determination of sheet size of graphene is very important for the production and application of graphene-based materials. However, the sizes of graphene and other 2D materials are not homogeneous. In view of the polydispersity and inhomogeneous of graphene sizes, methods have been used to characterize the size of graphene. Image method like optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and AFM are mostly used to indicate sheet sizes [14]. These methods have also been extended to measure other 2D materials like MoS2, WS2, TiS2, NbS2 and TaS2 [16, 17]. Besides, intrinsic properties can also be used to characterize graphene in typical sheet size range. Raman spectra have been used to measure the extinction, absorption, scattering that represent different lateral sizes ($90 \leq \langle L \rangle \leq 810nm$) and thicknesses ($2.7 \leq \langle N \rangle \leq 10.4$) of grapheme [18]. Among these methods, AFM is the most important and instrumental topographic analysis tool. Since the diameter of graphene sheet has been measured intuitively from the AFM image, the direct measurement method is generally used to obtain the lateral size of graphene. In this work, based on the AFM images, we demonstrate the lateral size calculation of graphene sheets using corresponding topographic height imaging and pixel data.

2. Method
Graphene oxide was provided by JCNANO Tech Co. Ltd. produced by a modified Hummers method. X-ray photoelectron spectroscopy (XPS) was performed on Thermofisher Escalab 250Xi. All binding energies were referenced to the C 1s neutral carbon peak at 284.8eV. The Raman spectra were recorded by using a Horiba's LabRam HR high resolution spectrometer. Atomic force microscopy (AFM) characterization was performed on a Bruker Dimension FastScan under tapping mode using FastScan-B probe with silicon tip on silicon nitride cantilever. Samples prepared by spin-coating GO onto silicon wafer substrate at 1000 rpm from diluted sample solutions.

3. Results and discussion
The Hummers method and its modified versions have been used to prepare GO and graphene by further chemical reduction. Using various acid solvent for graphite and different oxidant, GO with different degree of oxidation and sheet size have been achieved [19]. During the preparation process of GO, the introduced oxygen-containing functional groups gradually separate the oxidized graphene from the stacked graphite. At the same time, graphene oxide is mutually exclusive in solution due to the negative charge carried by the oxygen-containing functional groups on the surface. This ensures a single layer state in the dispersing system, which make GO a sample that is well suited for research and verification testing methods. Therefore, we choose GO as the research object in this paper.

Graphene oxide deposited on silicon wafer was direct observed by optical microscope. It can be observed that the GO sheets were spread evenly on the substrate (Figure 1a). High contrast between GO sheets and the substrate was not obtained due to the refractive index and optical absorption coefficient of GO, although single layer, bi-layer and multilayer graphene can be directly distinguished by optical microscope in reported works. From the Raman spectrum of the corresponding region, it can be seen that the GO on the silicon substrate is consistent with the macro-stacked GO results reported in the literature, and there is no change in the silicon substrate (Figure 1b).

The disorder-induced D band is observed at 1352.8cm-1, G band at 1352.8cm-1, the 2D band which peak intensity relative to the G band is much lower than that of the low defect graphene materials at 2702.3cm-1. The full range XPS analysis (Figure 1c) of the GO clearly shows the presence of carbon (C), oxygen (O) and nitrogen (N) with atomic percentages of 74.25%, 20.72% and 5.03%, and the corresponding C1s, O1s and N1s peaks centers at ~284.80eV, ~530.51eV and ~398.38eV, respectively. Accordingly, the GO had a molar ratio of carbon to oxygen atoms ([C] / [O]) of 3.58. The high-resolution C1s spectra of the GO are presented in Figure 1d as well.
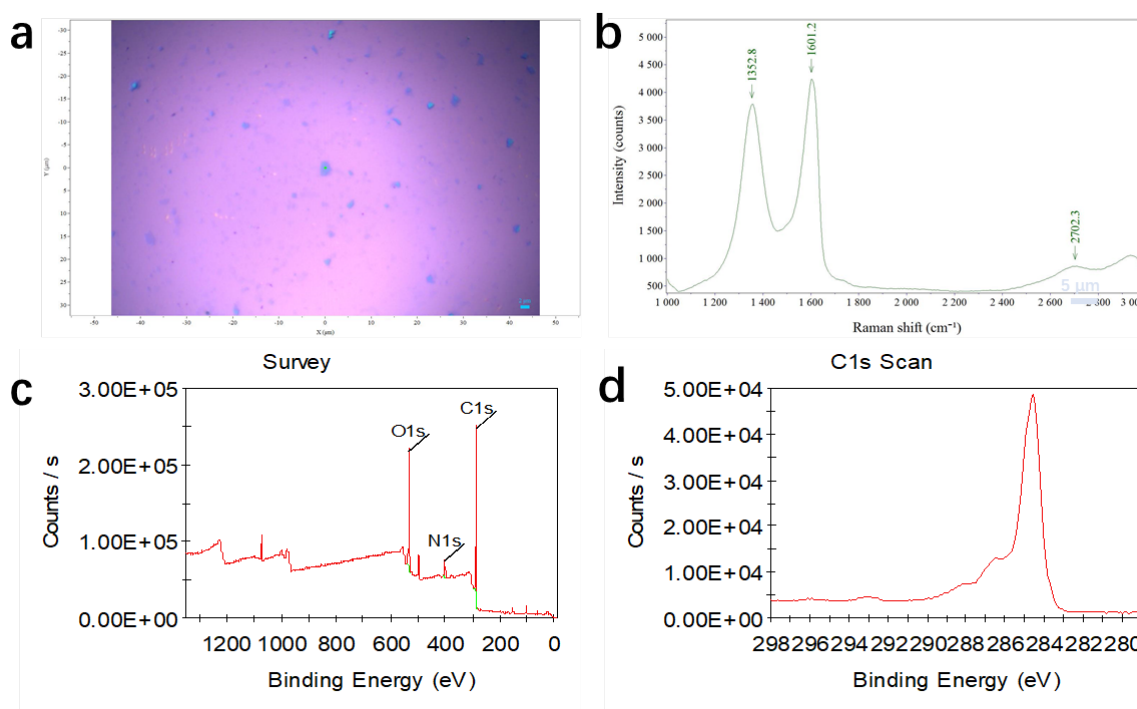

Figure 1. (a) Optical microscope picture of GO on the silicon substrate, (b) Raman spectrum of GO, (c) full-range XPS spectrum of GO, and (d) high-resolution C1s spectraum of GO.

AFM is commonly used to determine the thickness of graphene and related 2D materials. As it shown in Figure 2a, GO sheets spread evenly on the surface of the wafer, due to the difference in height and substrate of the area covered by the GO sheet, the morphology and height information of the sample can be clearly observed. The GO sheet has a measured thickness ranging from 0.68nm to 1.08nm and an average thickness of 0.929nm (Figure 2b). We chose to test a region where the GO sheets are relatively independent. By analyzing the height information, the 2D AFM picture can be converted into a 3D picture as shown in figure 2d. It can be seen from the 3D height map that the GO sheets have clear difference from the substrate, and by this difference in height, the area covered by the GO sheets can be more accurately calculated.

The AFM nanoscope analysis has two methods to analyze the size of the particles in the results based on the apparent height difference. The first one 'Width' is to analyze the width of features which measure the height difference between two dominant features that occur at distinct heights. In this way, one piece of GO sheet can be selected at a time, thereby obtaining the area of the coverage area. As it shown in Figure 3a, the lateral size of this GO sheet using the length of the largest circumscribed rectangle directly from the color difference of the image is 1.4μm. The area of the slice calculated using the 'Width' function is 1.4μm2, the lateral size is 1.047μm according to the equivalent square, and 0.591μm according to the equivalent circle (Figure 3b). At the same time, it can be seen from Figure 3c that the defective or low-height part inside the sheet is obviously not included in the result.
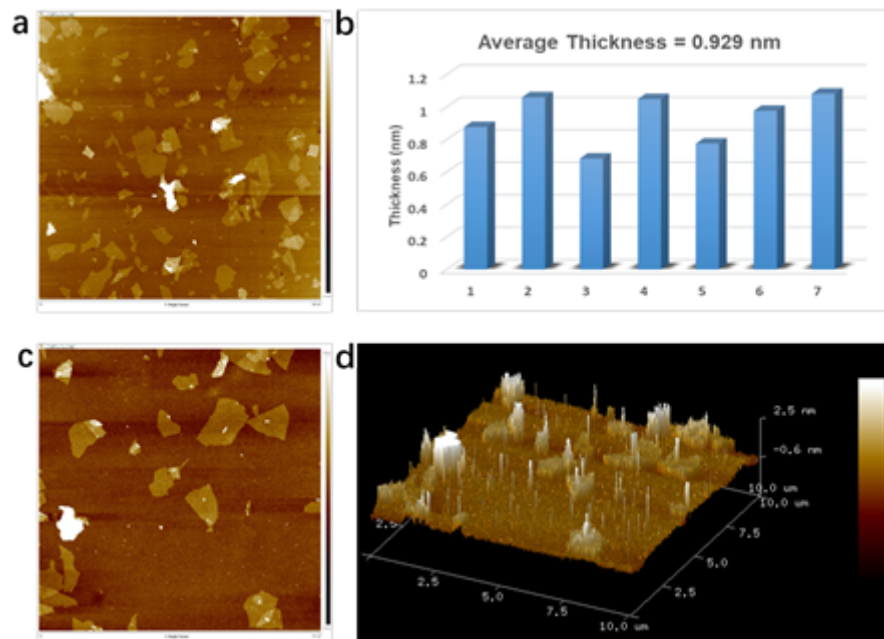
Figure 2. (a) AFM image of GO sheets in a large field of view, (b) Chart of GO thickness and its distribution, (c) AFM image of GO sheets in a small field of view, and (d) 3D AFM image including the height information.

Another method 'Particle Analysis' defines features of interest based on the height of pixel data. Different from Width just for only one graphene sheet, Particle Analysis designed for analyzing well isolated particles. As shown in Figure 3d, this method are conjoined pixels above or below a given threshold height and mark the area or particle that meets the requirements. In this way, the area of all the individual graphene sheets in the region can be calculated, but some small particles or impurities are also calculated and need to be artificially eliminated. In order to compare the difference between the height calculation and the direct measurement, we counted isolated GO sheets in the image (Figure 3e). The lateral size of GO sheets based on the height of pixel data ranging from 0.639μm to 1.357μm and an average value of 1.004μm according to the equivalent square. Using the direct measurement, the lateral size of GO sheets range from 0.877μm to 1.89μm and an average value of 1.365μm according to the length of the largest circumscribed rectangle, due to the elimination of the blank substrate area and the defect area, the lateral size obtained based on the height of pixel data is all significantly smaller than that by the direct measurement.

From the above process, calculate the lateral size by the height of pixel data is very convenient, and the following conditions must be met: 1. The average sheet size should be within the detection range of the AFM instrument, when the sheet size is too large, SEM or optical microscope can be used to test. 2. The preparation of the sample is very important, it is necessary to prepare a sample with well isolated particles on the surface of the substrate at a suitable concentration. 3. The flatness of the substrate must be guaranteed, or the substrate should be flattened by appropriate software functions during post-processing.
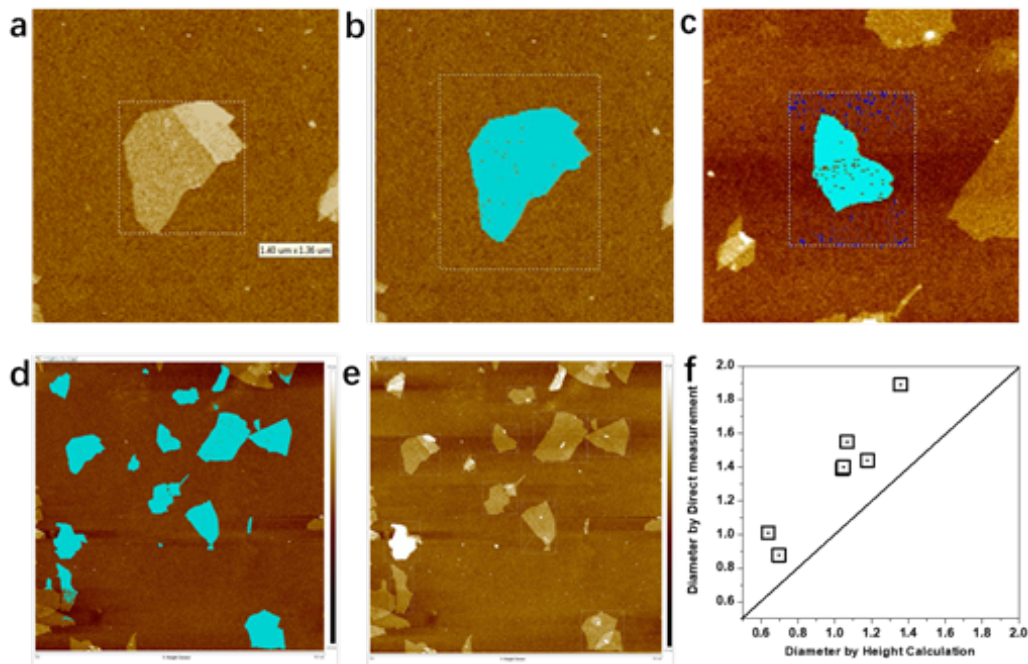
Figure 3. (a) direct measurement of lateral size of GO, (b) lateral size by measuring the height difference between two dominant features, (c) Chart of GO thickness and its distribution, (c) AFM image of GO sheets in a small field of view, and (d) 3D AFM image including the height information.

4. Conclusion

The lateral size of graphene oxide has been calculated using the height of pixel data provided by the AFM. This method based on the analysis of height data of sample is very accurate and convenient. The lateral size obtained based on this method is smaller than that by the direct measurement. This method is more suitable for the test of the lateral size in the AFM test range, and also the sample is prepared into with well isolated sheets. The method of calculating the lateral size and also sheet areas by the height data is important for obtaining the information of the sample by making full use of the results of the AFM. At the same time, this method can be applied to other 2D materials.

Acknowledgments

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