

Keysight Technologies

Friction, Phase and KFM Characterization of Functionalized Graphene Oxide

Application Note

Introduction

Graphene, as a two dimensional carbon sheet with hexagonal packed lattice structure, has been shown to possess unique electronic, optical, thermal and mechanical properties. Since the successful exfoliation of graphene layers by Novoselov et al¹ in 2004, interests on graphene and its chemically modified derivatives have grown significantly. Studies on their potential applications expanded to areas such as nanoelectronic devices, sensors, batteries, supercapacitors, solar cells, etc.² The applications of graphene are hindered, however, by the low throughput in mass production and the difficulty in making large and uniform sheets by mechanical exfoliation. Consequently, alternative synthetic methods by processes such as CVD and liquid exfoliation to overcome these problems become critical for the development of successful applications.³⁻⁵ Among them, the reduction of highly oxidized graphene sheet from liquid exfoliation of graphite oxide has become of particular interest. This is because the method not only provides a promising route to mass production of graphene oxide (GO) or reduced graphene oxide (rGO) sheets, but also

offers a platform for the production of a vast number of chemically modified graphene (CMG) sheets which can open the door to attractive material science applications.⁶⁻⁸

Graphene oxide sheets generated from exfoliation of oxidized graphite powder in liquid are enriched with oxygen containing groups such as epoxide (a cyclic ether with three ring atoms), hydroxyl (-OH), and carboxylic acid (-COOH).^{9,10} A schematic of the chemical moieties of GO is shown in Figure 1. These oxygen groups are all hydrophilic thus making the GO sheets highly water soluble. This ability to dissolve in water and other solvents allows GO sheets to be deposited uniformly on a range of substrates to make GO thin films in large scale.

Highly oxidized GO sheet is an insulator with higher roughness than its graphene counterpart. We have studied both graphene and GO with high resolution AFM imaging earlier.^{11,12} In average, the thickness of a single layer GO sheet is about 1nm, thicker than that of a single layer graphene which is less than 0.6nm. The observed increase in GO layer thickness comes from the oxygenated groups on the surface.

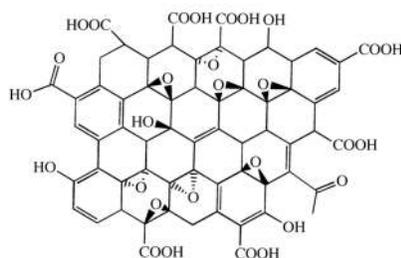


Figure 1. Graphene oxide (GO) is a water-soluble nanomaterial composed of planar, graphene-like aromatic domains of random sizes interconnected by a network of cyclohexane-like units in chair configuration which are decorated by hydroxy, epoxy, ether, diol, and ketone groups

Graphene oxide sheets can be reduced by chemical reagents such as hydrazine, vitamin C, hydriodic acid, etc. Reduced graphene oxide sheets show a significant increase in electric conductivity and a reduction of oxygen groups on the surface. The electric and optoelectric properties of the rGO sheets are tunable by controlling the degree of reduction.

The oxygenated groups on the GO and rGO surfaces act as the reactive sites for making CMG. For example, the hydroxyl groups can induce self-assembly of alkylsilanes. By selecting the silane species terminated with a desired functionality, the SAM layers can be used to tailor the chemistry at the GO/rGO surface. The difference in surface chemistry between GO/rGO and CMG will give rise to different physical properties. Here we will show the capability of characterizing GO/rGO surface properties using AFM imaging techniques such as friction, phase and single-pass KFM.

Sample

The chemically modified GO sample used for this study is prepared via the following steps: i) GO sheets are obtained by liquid exfoliation of highly oxidized graphite powder; ii) the GO sheets are functionalized by organosilane self-assembly that are terminated with carboxylic acid functional groups; and iii) the functionalized GO sheets are reduced by chemical reagents. As a consequence, multiple surface products could coexist after such a step-wise process.

SPM Characterization of SAM/GO Surface Chemistry

The sample has the following chemistry on the surface in theory: regions with SAM layer, regions with GO layer, and regions with reduced GO layer. It is well known that, in

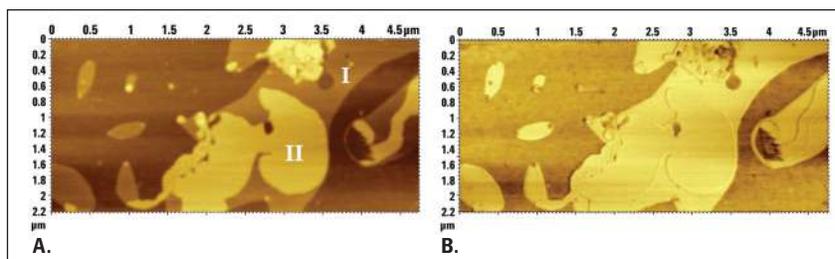


Figure 2. Topography (A) and friction (B) images of GO and organosilane functionalized GO imaged by contact mode AFM.

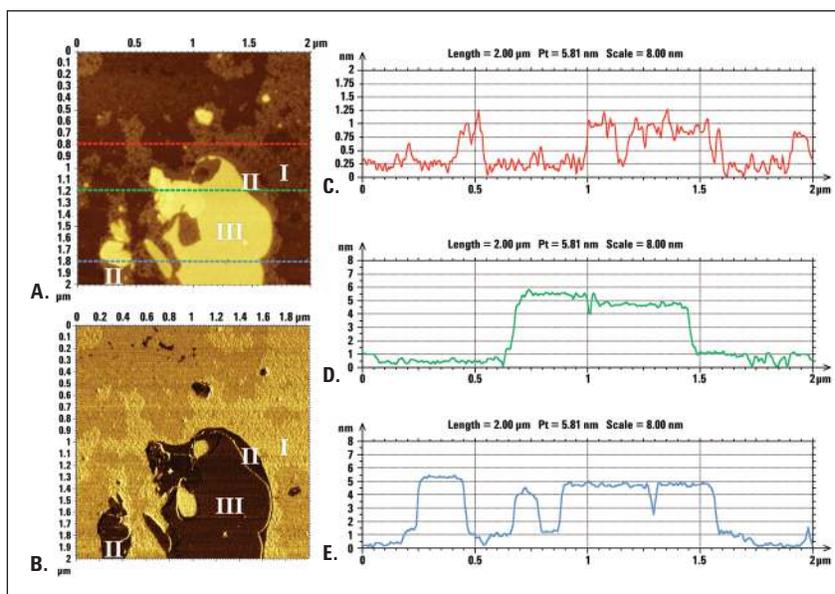


Figure 3. Topography (A) and phase (B) images of chemically modified GO/rGO. Domains labeled as I, II, and III correspond to GO layers with different chemical state. Line profiles corresponding to the dashed color lines are shown in (C), (D), and (E).

contact mode AFM, the friction between a Si_3N_4 tip and the sample surface depends on the chemical nature of the surface. Since both the SAM and GO regions on the sample are terminated with highly hydrophilic carboxylic and hydroxyl groups, they will show a higher force in the friction image comparing to the substrate and the rGO regions. The contact mode AFM images of the sample are presented in Figure 2. It shows regions, labeled I and II in Figure 2A, of different height on the topography, but having similar friction force (Figure 2B). The thickness of Region I is about 1 nm, corresponding to a single layer of GO/rGO. The thickness of Region II is about 3~4 nm. We have confirmed that the SAM layer is about 3.5 nm using AFM.¹² However, since both regions show similar

friction, it is insufficient to distinguish between SAM and GO based on only the topography data. It does, however, clearly show that the two regions are of similar chemical nature.

The topography and phase images from AAC mode are shown in Figure 3. From the topography image (Figure 3A) one can identify three regions of different thickness. Region I is a layer of about 1 nm in thickness, with patches of holes and trenches across the surface. Figure 3C shows a profile of Region I along the red line in Figure 3A. It is known that GO sheets possess a certain degree of atomic disorder and even large defects upon reduction.¹⁰ Therefore Region I in Figure 3A can be attributed to regions of rGO that are highly reduced. The phase of this

region is very close to that of the mica substrate.

Region II in Figure 3A is similar to Region I in thickness, see line profile in Figure 3D. However, the phase signals between the two regions are significantly different. It is also observed that Region II is smooth and perfectly packed as compared to Region I. As a result, it is reasonable to conclude that Region II corresponds to a single layer of the GO sheet, left behind from the reduction.

There are a number of areas having similar height in the topography image (Figure 3A), and are labeled Region III. A line profile across them (indicated by the blue dashed line in Figure 3A) is plotted in Figure 3D. The height difference between Region II and III is about 3 nm, close to the measured thickness of the organosilane SAM layer. The phase image also shows that the two regions have similar surface chemistry, consistent with the friction image discussed earlier. A closer look at Figure 3A revealed that there existed a small height difference between two parts of Region III, also visible on the line profile in Figure 3D. The height difference is estimated about 1 nm, corresponding to a single layer of GO or rGO. In order to identify the chemical nature of the region, SAM or GO, surface potential measurement was performed on the same sample.

Figure 4 shows the KFM measurement over an area where the thickness of the sheets is about 4 nm, with scattered holes over the surface. The tall islands on the topography (Figure 4A) are contaminants from the preparation. It is clearly shown that the surface has a distinct potential difference from the holes (Figure 4B). The potential difference estimated from the line profile (Figure 3D) is about 130 mV. Figure 3C is the corresponding dC/dZ image which shows a weak difference between the GO sheets and the

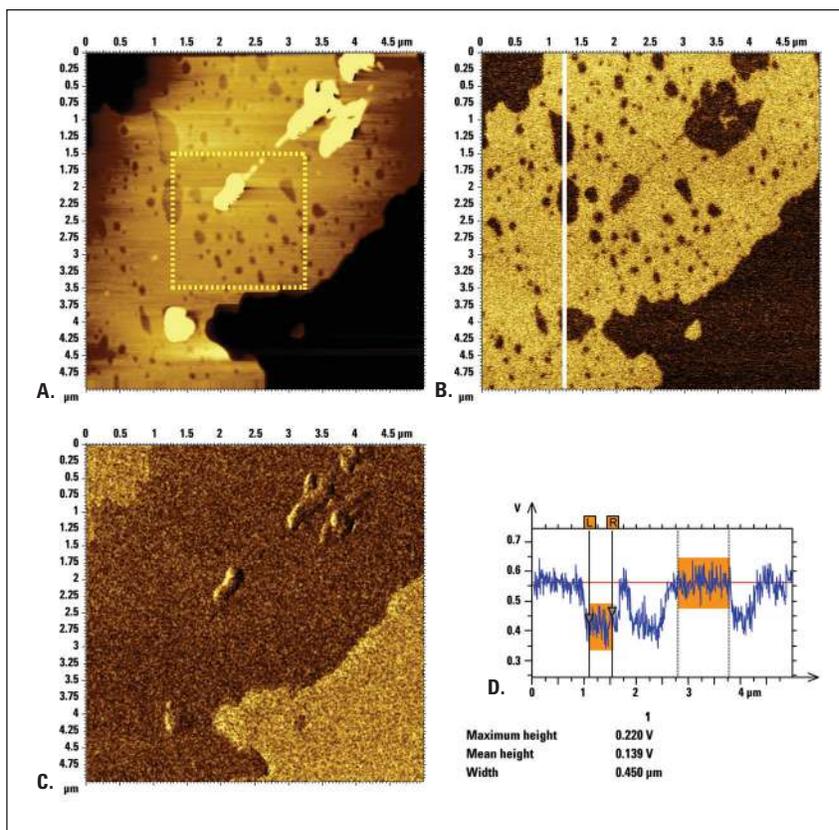


Figure 4. Topography (A), Surface Potential (B) and dC/dZ (C) images of multilayers of GO showing holes in the top layer due to chemical reduction. Line profile indicated by the vertical line in (B) is presented in (D).

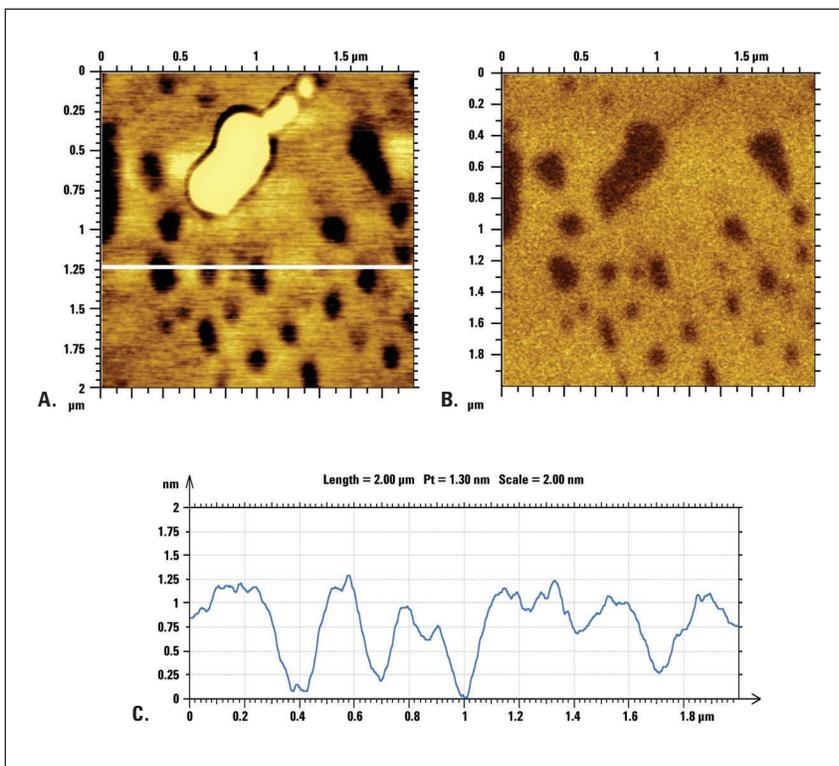


Figure 5. Topography (A) and surface potential (B) images of the region indicated by the yellow dotted frame in Figure 4A. Line profile (C) shows the depth of the holes is inconsistent with the thickness of a single layer GO.

mica substrate. Figure 5 presents a close-up scan of the area indicated by the yellow dotted frame in Figure 4A. From the measurement done over the line profile (Figure 5C), one can estimate the depth of the holes, or the thickness of the top layer, is about 1 nm. Therefore, the GO sheets shown in Figure 5 are from multilayers of GO with the top layer reduced to rGO. The holes from extreme reaction further confirm this point. The negative potential in the 'holes' corresponding to a more negative surface charge, suggesting the underneath layers contain more oxygen than the top rGO layer.

Due to the fact that organosilane are covalently bound to the GO as well as the strong cross-linking (covalent bond too) between the silane molecules, the SAM layers are inert to chemical reduction in this system and maintain its structural integrity. Therefore, Region III in Figure 3A corresponds to a self-assembled organosilane layer, due to the robustness of the organosilane, showing a densely packed surface without defects caused by chemical reduction.

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Summary

Friction, phase and KFM imaging are performed on a number of chemically modified GO sheets. The capability of characterizing the chemical nature of the CMG is demonstrated by detailed analysis of the results from those images. It also demonstrates that the combination of different techniques in SPM makes it a powerful tool in characterizing GO and its chemical derivatives.

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Keysight Technologies, Inc. offers high-precision, modular AFM solutions for research, industry, and education. Exceptional worldwide support is provided by experienced application scientists and technical service personnel. Keysight's leading-edge R&D laboratories are dedicated to the timely introduction and optimization of innovative and easy-to-use AFM technologies.

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