

Graphene Oxide and Its Applications Revealed by Atomic Force Microscopy

Application Note

Jing-jiang Yu and Boon-Keat Chong
Agilent Technologies

Introduction

The successful preparation and verification of a mechanically exfoliated graphene monolayer by Novoselov *et al.* in 2004 has generated huge sensation and fueled the exponential growth of research on graphene-related materials.¹ Recently, graphene oxide (GO) has attracted tremendous attention, owing to the escalating demands for seeking scaled-up production of graphene and exploring their potential applications in various technological fields. Different from graphene that is a single-layer sheet composed purely by carbon atoms with a hexagonal lattice structure, the individual GO sheet is enriched with oxygen-containing groups such as epoxide (a cyclic ether with three ring atoms), hydroxyl (-OH) or carboxylic acid (-COOH) groups, and is highly soluble in water. As a consequence, a proposed three-step approach, i.e.; 1) Synthesis of graphite oxide from pristine graphite powder; 2) Exfoliation of graphite oxide in water to generate a dispersion of single-layer graphene oxide; and followed by 3) A chemical or thermal reduction of graphene oxide to graphene; opens up a promising route to achieve large-scale production of graphene. On the other hand, these reactive terminal functionalities can serve as the initial binding sites to direct well-controlled surface interactions, thus to achieve either a designed functionalization of graphene oxide or constructions of hierarchically structured graphene materials.

In this application note, above-mentioned interfacial chemistry as both an intrinsic nature of GO materials and a key driving force for directing their applications will be characterized and illustrated from a microscopic point of view, using atomic force microscopy (AFM) as the main technique.

High-resolution AFM Imaging of Single-layered Graphene Oxide Nanosheets

Controlled synthesis of graphene or its derivatives with a desired number of layer ($n=1$) is still a challenge. The existing approaches to yield graphene include mechanical exfoliation, chemical vapor deposition, and chemical or thermal reduction of graphite oxide. Among them, the last one is considered to be the most economical way to produce a large quantity of graphene. Due to the hydrophilicity and ionizability of its oxygen-containing functional group, graphite oxide can be readily exfoliated in water to yield stable dispersions of single GO layers. Such behavior potentially allows the large-scale preparation of single-layer graphene and is verified by our AFM characterization. After spin-casting a solution of dispersed GO nanosheets onto a mica substrate, the resulting surface morphology is examined directly using high-resolution AFM imaging. As can be seen from Figure 1, the planar nature of GO sheets allows them to be in good contact with the flat substrate

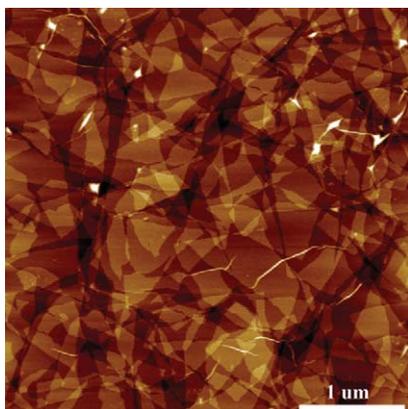


Figure 1. High-resolution AFM imaging of single-layered graphene oxide (GO) nanosheets absorbed on a mica substrate. Scan size: $4\ \mu\text{m} \times 4\ \mu\text{m}$.

as well as the stacking of GO layers. All GO are orientated parallel to the mica and packed firmly into a multi-layer structure. More importantly, these absorbed GO sheets exhibit good uniformity in term of their thickness. A quantitative probing on that is achieved via the AFM height measurements. Figure 2 (top) is a typical and more close-look view of the surface, in which a blue cursor line is drawn at a particular location where three levels of heights due to the various stacking of GO films are clearly resolved. The corresponding cross-section profile (Figure 2, bottom) indicates that the apparent heights of those steps are about 1 nm, which is in good agreement with the theoretical value of a single GO layer. Therefore, it strongly suggests that most of GO ultrathin films are actually single-layered GO sheets.

Previously, we also studied single-layer and few-layer graphene materials using AFM. In contrast, the measured apparent height of single-layer graphene is less than 0.6 nm.² The observed increase in thickness for a single layer GO can be attributed to the introduction of the additional functionalities on top of graphene. Herein, it proves the capability of differentiating GO layer from graphene or reduced graphene oxide (rGO) via high-resolution AFM imaging and height measurements.

Graphene-metal Nanoparticle Composites

GO can be defined as a special nanomaterial with 1) incredibly large surface area owing to the two accessible sides; and 2) rich interfacial chemistry due to the surface functionalities such as epoxide, hydroxyl and carboxylic groups, which could potentially facilitate or direct the deposition of metal nanoparticles, organic macromolecules and even some biological species. For example, graphene oxide as a matrix for enzyme immobilization has been reported. Without using any cross-linking reagents and additional surface modification, those abundant surface terminal groups make the adsorption of the protein molecules quickly

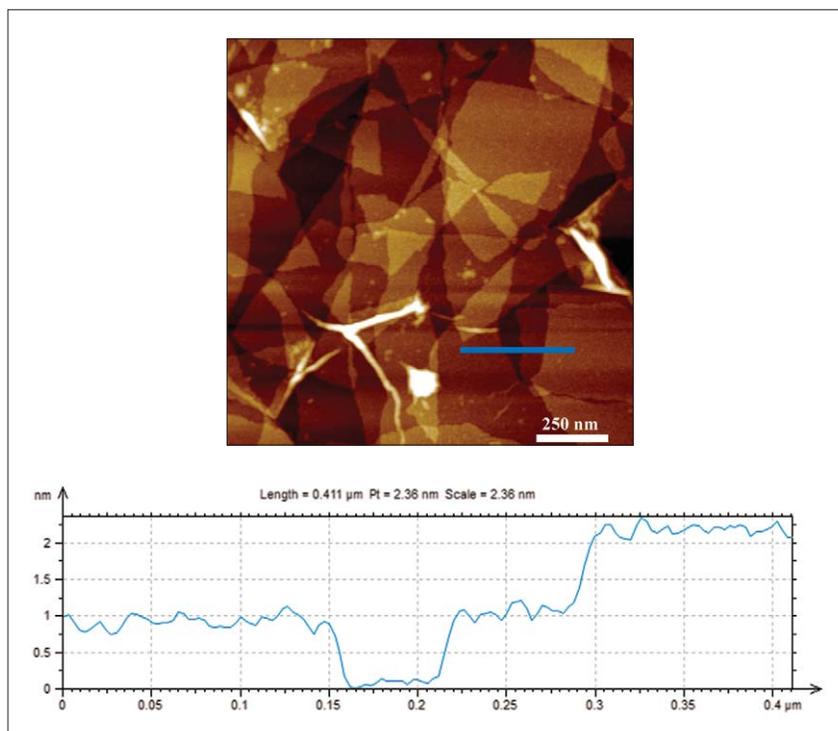


Figure 2. Quantitative thickness measurements of single-layered GO. (Top) An AFM topographic image that allows a closer look of individual GO layers. Scan size: 1.5 μm × 1.5 μm. (Bottom) The cross-section profile corresponding to the blue line drawn in the topographic image.

through electrostatic interactions and those proteins maintain their specific bioactivity afterwards.³

Regarding the fabrication of GO with metal nanostructures, various approaches ranging from *ex situ* hybridization to *in situ* crystallization have been developed. Particularly, the chemical reduction method is the most popular strategy. Precursors of noble

metals such as HAuCl₄, AgNO₃, K₂PtCl₄ and H₂PdCl₆ can be simply reduced by agents like amines, NaBH₄, and ascorbic acid.⁴ An example of successful preparation of GO-Ag nanoparticle composite is shown in Figure 3. The binding of silver nanoparticles onto GO sheets is evidenced by both topography (Figure 3, left) and phase image (Figure 3, right).

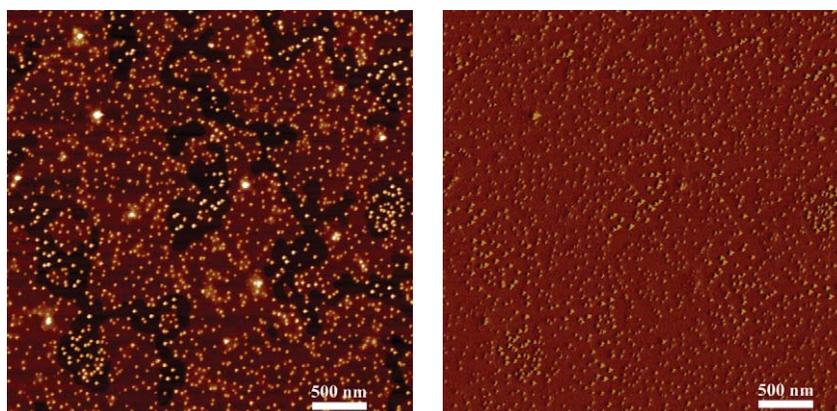


Figure 3. High-resolution topography (left) and corresponding phase (right) images of GO-silver nanoparticle composites. Scan size: 4 μm × 4 μm.

Functionalization of GO via Organosilane Self-assembly

Construction of graphene-related materials with a designed or even tunable chemistry is critical for their applications in wide varieties of fields such as biosensing, solar cells and nanocomposites. During recent decades, organosilanes on silica and alkanethiols on gold have been fully developed as two model systems of self-assembled monolayers (SAMs). In fact, one of the key advantages associated with SAMs is their rich endgroup chemistry. By simply selecting a silane or thiol species terminated with a desired functionality, these self-organized organic thin films can be used readily to tailor the interfacial chemistry of a surface. In fact, the spontaneous and covalent binding of organosilane molecules on fused silica results from a silanol-based chemical reaction and formation of organosilane SAMs could, in principle, occur on other hydroxyl-containing substrates such as graphene oxide. Therefore, combining GO with organosilane self-assembly render an effective means to obtain functionalized GO, which can serve as the building block for further synthesis of hierarchically structured graphene materials.

A successful example of achieving functionalization of GO via organosilane self-assembly is presented here. Figure 4 is a schematic illustration of the surface reaction between GO and a specific type of organosilane. After the mixing of them in a solution, the resulting products were deposited onto mica and visualized directly by AFM. Except the unoccupied substrate areas, two different surface features are observed in AFM topographic image (Figure 5, top). Those regions (labeled as **I**) are very smooth and slightly higher than the mica substrate. Cross-section profile (Figure 5, bottom) shows that their apparent heights are about 1 nm, indicating that they are single-layer GO sheets unreacted after the soaking in the organosilane solution. In comparison, the other regions (labeled as **II**) exhibit a much rougher morphology and some surface defects. They are about 3 nm higher than

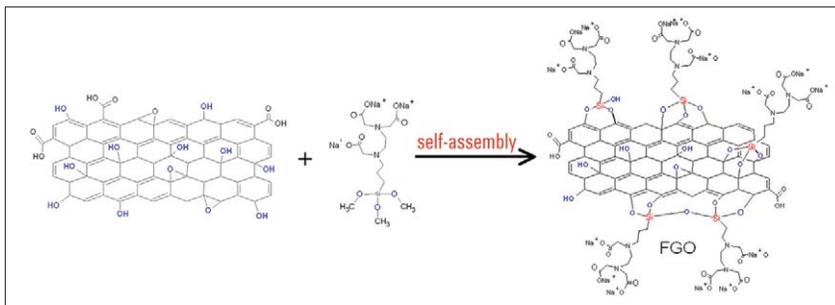


Figure 4. A schematic illustration of the self-assembly of organosilanes onto GO.

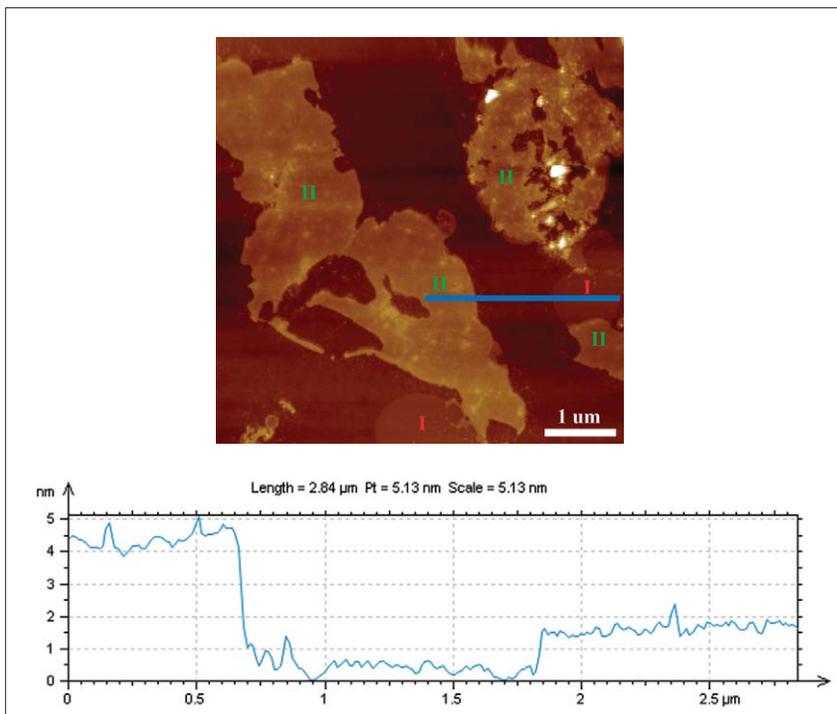


Figure 5. Chemical functionalization of GO via organosilane self-assembly. (Top) An AFM topographic image showing the coexistence of the resulting GO-silane complex and some unreacted GO sheets. Scan size: $6\ \mu\text{m} \times 6\ \mu\text{m}$. (Bottom) The cross-section profile corresponding to the blue line drawn in the topographic image.

the GO sheets. This increased height is consistent to the theoretical value of the length of organosilane molecules or their multilayered structures. As a result, the AFM studies provide a strong experimental evidence to prove the successful binding of organosilane onto GO.

Summary

The capability of atomic force microscopy as a powerful tool in characterization of GO and its derivatives is demonstrated in the note. High-resolution imaging and

height measurements allow the identification of GO from graphene or reduced GO. In addition, two GO-related research areas, synthesis of graphene-inorganic nanostructure composites and functionalization of graphene via self-assembly of selected organosilanes onto GO, were studied using AFM.

Acknowledgement

All of the samples studied in this application note were kindly provided by Dr. Vijay Kumar and Prof. Nay Ming Huang from University of Malaya.

References

1. Novoselov *et al.* "Eclectic field effect in atomically thin carbon films" *Science* **2004**, *306*, 666–669.
2. Yu *et al.* "Thickness-dependent electrical properties of single-layer graphene and few-layer graphene: a Kelvin force microscopy study" *Application Note 5990-4516EN*. **2012**, Agilent Technologies, Inc.
3. Zhang *et al.* "Graphene oxide as a matrix for enzyme immobilization" *Langmuir* **2010**, *26*, 6083–6085.
4. Huang *et al.* "Graphene-based composites" *Chem. Soc. Rev.* **2012**, *41*, 666–686.

AFM Instrumentation from Agilent Technologies

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

www.agilent.com/find/afm

Americas

Canada	(877) 894 4414
Latin America	305 269 7500
United States	(800) 829 4444

Asia Pacific

Australia	1 800 629 485
China	800 810 0189
Hong Kong	800 938 693
India	1 800 112 929
Japan	0120 (421) 345
Korea	080 769 0800
Malaysia	1 800 888 848
Singapore	1 800 375 8100
Taiwan	0800 047 866
Thailand	1 800 226 008

Europe & Middle East

Austria	43 (0) 1 360 277 1571
Belgium	32 (0) 2 404 93 40
Denmark	45 70 13 15 15
Finland	358 (0) 10 855 2100
France	0825 010 700*
	*0.125 €/minute
Germany	49 (0) 7031 464 6333
Ireland	1890 924 204
Israel	972-3-9288-504/544
Italy	39 02 92 60 8484
Netherlands	31 (0) 20 547 2111
Spain	34 (91) 631 3300
Sweden	0200-88 22 55
Switzerland	0800 80 53 53
United Kingdom	44 (0) 118 9276201

Other European Countries:

www.agilent.com/find/contactus

Product specifications and descriptions in this document subject to change without notice.

© Agilent Technologies, Inc. 2012
Printed in USA, June 27, 2012
5991-0795EN



Agilent Technologies