



Direct observation of oxygen configuration on individual graphene oxide sheets



Zilong Liu ^a, Kasper Nørgaard ^a, Marc H. Overgaard ^a, Marcel Ceccato ^a,
David M.A. Mackenzie ^b, Nicolas Stenger ^c, Susan L.S. Stipp ^a, Tue Hassenkam ^{a,*}

^a Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100, Copenhagen, Denmark

^b Center for Nanostructured Graphene (CNG), Department of Micro- and Nanotechnology, Technical University of Denmark, Ørstedes Plads 345 B, Kongens Lyngby, 2800, Denmark

^c Center for Nanostructured Graphene (CNG), Department of Photonics, Technical University of Denmark, Ørstedes Plads 345 A, Kongens Lyngby, 2800, Denmark

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ABSTRACT

Graphene oxide (GO) is an interesting material that has the potential for a wide range of applications. Critical for these applications are the type of oxygen bond and its spatial distribution on the individual GO sheets. This distribution is not yet well understood. Few techniques offer a resolution high enough to unambiguously identify oxygen configuration. We used a new, label free spectroscopic technique to map oxygen bonding on GO, with spatial resolution of nanometres and high chemical specificity. AFM-IR, atomic force microscopy coupled with infrared spectroscopy, overcomes conventional IR diffraction limits, producing IR spectra from specific points as well as chemical maps that are coupled to topography. We have directly observed oxygen bonding preferentially on areas where graphene is folded, in discrete domains and on edges of GO. From these observations, we propose an updated structural model for GO, with C=O on its edge and plane, which confirms parts of earlier proposed models. The results have interesting implications. Determining atomic position and configuration from precise imaging offers the possibility to link nanoscale structure and composition with material function, paving the way for targeted tethering of ions, polymers and biomaterials.

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1. Introduction

One of the limitations for more extensive use of graphene-based materials is the challenge of mass production but graphene oxide (GO) has been widely adopted as a starting material for material synthesis [1,2] and there is potential for many more technological applications [3–6], such as optoelectrical and electronic devices, heterogeneous catalysis, polymer composites as well as in biomedicine and biotechnology. Because GO is covalently decorated with oxygen on its plane and edges [7], it is hydrophilic, which makes fabrication of graphene containing devices from solution both economical and practical. Perhaps most important, the aromatic scaffolds and the oxygen networks on GO provide abundant anchoring sites for functionalization by ions, polymers, nanoparticles and biological species [5,6].

In the aim of tailoring the fundamental properties of GO, to unleash its potential for applications, detailed understanding of atomic composition and bonding is required. The ideal graphene structure, a single layer of sp^2 bonded carbon atoms arranged in a honeycomb motif, is well known. However, once oxidized, GO restructures so the atomic arrangement becomes heterogeneous, affecting its composition and chemical properties. The unresolved questions are: What is the distribution of oxygen bonding on GO? And how does this affect the underlying carbon template? An accurate structural model is a prerequisite for predicting reactivity. Uncertainty remains because the ultrathin GO layers make analysis difficult. Several spectroscopic approaches have been used to investigate the type, abundance and distribution of oxygen that is chemically bonded to the carbon network. Such techniques include nuclear magnetic resonance (NMR) [7–9], X-ray absorption near edge spectroscopy (XANES) [10], Raman spectroscopy [11], X-ray photoelectron spectroscopy (XPS) [12,13], and Fourier transform infrared spectroscopy (FTIR) [12,14–16].

Based on data from NMR with isotope labelling, the most widely

* Corresponding author.

E-mail address: tue@nano.ku.dk (T. Hassenkam).

used structural model of GO was proposed by Lerf-Klinowski (LK) [7]. In this model, oxygen is bonded singly to the GO carbon plane, in configurations reminiscent of epoxy and hydroxyl, which provide structural rigidity to GO, while oxygen is bonded singly and doubly on the edges, as in carboxyl, and these oxidized groups give rise to its solubility in water. The general model has not changed much since it was proposed but more recent results [8] have triggered modifications, such as addition of oxygen in other configurations, as in ketones, lactols and ester carbonyls. The model was further improved by the results from a set of experiments that revealed simple spatial connectivity between regions with oxygen in epoxide and hydroxyl arrangements [9]. Use of other analytical techniques has also provided indirect evidence that is consistent with the LK model [10,17–19].

With XANES, the various carbon bonding environments for oxygen were explored, to resolve the composition and structure of GO [10]. Results confirmed the essence of the LK model but could only provide a macroscopic perspective, i.e. data averaged over many surfaces. In other studies, the oxidized and unoxidized areas of GO have been explored using high resolution transmission electron microscopy (TEM) [17] and electron energy loss spectroscopy (EELS) [18,19], providing proof that oxygen atoms are randomly attached to GO sheets, converting carbon bonds from sp^2 to sp^3 . Other spectroscopic techniques [11–16], mainly Raman, XPS and FTIR, have provided information about oxygen bonding neighbours and their relative proportions but details about the actual spatial distribution of oxygen and its bonding types on GO, at the nanometer scale, has not been possible.

Our purpose was to map the spatial distribution of C–O and C=O bonds on GO and use the direct experimental observations from the nanometer scale to propose a more robust structural model. We characterized GO and identified the location of oxygen and the type of bonding using a new technique: AFM-IR [20–22]. It combines atomic force microscopy with a pulsed IR laser that is tuneable over the mid IR range ($900\text{--}3600\text{ cm}^{-1}$). It allows IR spectroscopy at AFM resolution, namely tens of nanometres in x and y and 0.1 nm or less in z . This resolution is not possible with standard, optical IR because of the diffraction limit but by combining the best of two worlds, we can visualize oxygen bonding on GO with near molecular resolution.

2. Experimental

2.1. Sample preparation

Commercial graphite powder (Grade 3061) was obtained from Asbury Carbon Mills. H_2SO_4 (95–98%), KMnO_4 and H_2O_2 (33%) were obtained from Sigma Aldrich and NaNO_3 was obtained from Merck. All were reagent grade or better and were used as received.

GO was prepared by harsh oxidation of the graphite powder by the modified Hummers method [23,24]. In a typical reaction, we put 1 g graphite and 0.5 g NaNO_3 into a round bottomed flask and added 24 mL of concentrated H_2SO_4 . The mixture was placed on ice and stirred for 5–10 min, then 6 g KMnO_4 was added in small portions over a period of 30 min. The reaction mixture was stirred on ice for 2 h more. The flask was then transferred to an oil bath, preheated to $35\text{ }^\circ\text{C}$ and left to oxidize for 16 h. Reaction refinement and purification were initiated by adding 40 mL ultrapure deionised water dropwise into the reaction mixture under stirring, which was then briefly heated to $90\text{ }^\circ\text{C}$ for 5 min. The reaction vessel was allowed to cool to room temperature and 100 mL ultrapure water was added in one portion. Oxidation was terminated by adding 4 mL H_2O_2 (33%) dropwise into the flask.

The freshly synthesized GO was rinsed 5 times with ultrapure water and centrifuged, to remove residual acid and salts. Typically,

4–6 repetitions were sufficient to achieve proper washing, which was tested by measuring pH of a neutral supernatant. The material was delaminated by mild sonication for 4 min and centrifugation at 2000 rpm until no visual sedimentation was observed. Finally, the GO was centrifuged twice at 9000 rpm to remove oxidative debris [25], which are small size functionalized graphene rich in oxidized groups. For each experiment, a $30\text{ }\mu\text{L}$ aliquot of the GO solution was deposited on a clean gold substrate and dried in a stream of clean nitrogen gas.

2.2. X-ray photoelectron spectroscopy

The chemical state and the element composition of GO were determined with XPS (Kratos Axis Ultra DLD), using monochromatized $\text{Al K}\alpha$ ($h\nu = 1486.6\text{ eV}$) as the excitation source [26]. The data were analyzed using commercial software, CasaXPS, and a Shirley background fit. The carbon peaks were referenced to $285.0 \pm 0.1\text{ eV}$ [13]. Uncertainty in XPS binding energy is about 0.1 eV . Uncertainty in the atomic percentages determined from XPS data is on the order of 5–10%.

2.3. Raman spectroscopy

Raman spectroscopy was performed using a Thermo Scientific DXRxi fitted with a 532 nm laser. Using a laser power of 3 mW, 180 Hz collection frequency was scanned 900 times per pixel through at $100\times$ objective.

2.4. Fourier transform infrared spectroscopy

We used a FTIR Vertex v70 from Bruker coupled to a infrared microscope Hyperion 2000 for micro-FTIR measurements. The light source is a SiC “glowbar” and we measured in reflection and transmission modes. The detector is a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector. The measurement window was $900\text{--}2000\text{ cm}^{-1}$ and $2500\text{--}3600\text{ cm}^{-1}$ range. We averaged over 128 spectra with a spectral resolution is 4 cm^{-1} .

2.5. Infrared nanospectroscopy using AFM-IR

The localized nanoscale mid-IR spectra were collected using a nanoIR2 instrument (AFM-IR) from Anasys Instruments, Inc. It consists of an AFM with a pulsed, tunable IR laser. With AFM-IR, one can generate topographic images of GO with the AFM and it also serves as a nearfield detector for measuring the absorption of IR radiation. In mapping mode, one sets the laser at a specific wavelength and collects absorption intensity data over a selected area. Spatial resolution is about 40 nm per pixel. In spectra mode, one can acquire IR spectra at specific sites while ramping the energy of the laser.

With the tunable IR sources on our instrument, pulse length is about 10 ns and energy ranges over the middle IR region ($900\text{--}3600\text{ cm}^{-1}$). In Supplementary Fig. S1A, it shows the principles of the technique based on the photothermal induced resonance effect [20,21]. When IR radiation is absorbed by a sample, it heats, causing an almost instantaneous thermal expansion that induces oscillations of the AFM cantilever. The oscillations decay in a ringdown mode (Supplementary Fig. S1B), which typically contains multiple frequencies and amplitudes (Supplementary Fig. S1C). Because sample expansion is much faster than AFM feedback (typical laser repetition rate 1 kHz), it allows sufficient time for completing a ringdown and exciting resonant modes of the AFM cantilever before a new pulse arrives. The ringdown is usually analyzed by Fourier transform, to extract the useful information. The resonant amplitudes in the cantilever are proportional to the intensity of the

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