



ELSEVIER

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Atomic resolution imaging and spectroscopy of barium atoms and functional groups on graphene oxide

C.B. Boothroyd^{a,*}, M.S. Moreno^b, M. Duchamp^a, A. Kovács^a, N. Monge^c, G.M. Morales^c, C.A. Barbero^c, R.E. Dunin-Borkowski^a

^a Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, D-52425 Jülich, Germany

^b Centro Atómico Bariloche, 8400 – San Carlos de Bariloche, Argentina

^c Department of Chemistry, Universidad Nacional de Río Cuarto, X5804BYA Río Cuarto, Argentina

ARTICLE INFO

Article history:

Received 2 October 2013

Received in revised form

9 February 2014

Accepted 8 March 2014

Keywords:

Graphene oxide

Functional groups

Scanning transmission electron microscopy

Transmission electron microscopy

Spectrum imaging

Atomic resolution

Single atom imaging

ABSTRACT

We present an atomic resolution transmission electron microscopy (TEM) and scanning TEM (STEM) study of the local structure and composition of graphene oxide modified with Ba²⁺. In our experiments, which are carried out at 80 kV, the acquisition of contamination-free high-resolution STEM images is only possible while heating the sample above 400 °C using a highly stable heating holder. Ba atoms are identified spectroscopically in electron energy-loss spectrum images taken at 800 °C and are associated with bright contrast in high-angle annular dark-field STEM images. The spectrum images also show that Ca and O occur together and that Ba is not associated with a significant concentration of O. The electron dose used for spectrum imaging results in beam damage to the specimen, even at elevated temperature. It is also possible to identify Ba atoms in high-resolution TEM images acquired using shorter exposure times at room temperature, thereby allowing the structure of graphene oxide to be studied using complementary TEM and STEM techniques over a wide range of temperatures.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of graphene, a huge effort has been made to study graphene oxide (GO), as it is the most promising precursor for producing graphene on a large scale at low cost. In addition, GO and reduced graphene oxide (rGO), in which the C:O ratio is higher than in as-synthesised GO, are versatile and functional materials in themselves for a number of applications that include catalysis, sensing, optical imaging for biological applications and solar cells [1–5].

GO is usually described as a distribution of individual sheets of graphene with oxidised domains, where oxygen-containing functional groups (such as alcohols, epoxy groups, carbonyl groups, hydroxyl groups, carboxylic acids, peroxide, ketones and quinones) are anchored to both sides of the sheet [6,7]. The functionality of GO and rGO results from the extensive presence of these groups,

which are suitable for chemical functionalisation [6]. The presence of functional groups necessarily implies that there are defects in the hexagonal graphene lattice, which act as anchoring sites for atoms or groups other than C. At such defect sites, the sp² hybridisation of the graphene lattice is not preserved. In general, GO and rGO are considered to be non-stoichiometric materials because the density of oxygenated functional groups and defects cannot be controlled [8–11]. As the high reactivity of GO allows for additional manipulation by controlled chemical functionalisation [12], a broad variety of possibilities that involve non-covalent, covalent or coordinate bonding are available for tailored applications. For example, modification of GO with cations by coordinate bonding has been used to enhance its mechanical properties [13] and to produce gel-like 3D structures [14,15].

Despite its importance, the chemical structures of GO and rGO are still unclear, in part because the compositions and distributions of the functional groups depend on the specific conditions and synthesis methods that are used. The chemical compositions and spatial distributions of the functional groups are of particular importance because they determine most of the properties of both GO and rGO. Most previous work has involved the use of spectroscopic techniques, which provide information that is averaged over a large area of the specimen. For example, it has been reported using infrared and X-ray photoelectron spectroscopies

Abbreviations: TEM, transmission electron microscopy; HRTEM, high-resolution transmission electron microscopy; STEM, scanning transmission electron microscopy; ADF, annular dark-field; HAADF, high-angle annular dark-field; EFTEM, energy-filtered transmission electron microscopy; GIF, Gatan imaging filter; GO, graphene oxide; rGO, reduced graphene oxide; VCA, vertex component analysis

* Corresponding author. Tel.: +49 2461 619279.

E-mail address: ChrisBoothroyd@cantab.net (C.B. Boothroyd).

<http://dx.doi.org/10.1016/j.ultramic.2014.03.004>

0304-3991/© 2014 Elsevier B.V. All rights reserved.

that thermal reduction of GO occurs in vacuum, changing the C:O ratio [16–18]. More recently, ultrafast optical spectroscopy has been used to determine that GO consists of graphene-like domains surrounded by oxygen-rich areas [8].

High-resolution transmission electron microscopy (TEM) and scanning TEM (STEM) can be used to reveal the presence of both ordered regions and amorphous materials in GO. The amorphous areas are assumed to be highly defective regions in the substrate, to which functional groups are anchored [19,20]. However, the direct identification of individual functional groups has not been possible, as it is not straightforward to distinguish them from amorphous contaminants or to identify individual C and O atoms.

One approach that can be used to identify functional groups in GO and to map their positions is to modify the GO using metal ions, such as Ba^{2+} or Cs^+ , which interact selectively with specific oxygen-containing groups. Barium ions can form complexes with oxygen-containing groups either on their own [21] or in combination with carboxylates [22] or carbonyl groups [23]. The complexes with carboxylate groups are strong enough to build coordination polymers [24]. Therefore, it is likely that Ba^{2+} ions attach by interaction with the carbonyl, epoxy and carboxylate groups on the surface of GO, but are more strongly attached to the carboxylate groups, making selective staining of these groups possible. The distribution of the heavy atoms, which provide distinct contrast in both high-angle annular dark-field (HAADF) STEM and high-resolution transmission electron microscope (HRTEM) images, rather than the functional groups themselves, can then be imaged. Although Bai et al. [15] modified GO with heavy ions such as Ag^+ and Pb^{2+} , we believe that the results that we present below provide the first example of the modification of GO using heavy atoms specifically for the purpose of attempting to visualise oxygenated groups in GO. Moreover, the chemical natures of Ba^{2+} and Cs^+ make it very unlikely they will be reduced to metal (to form nanoparticles), whereas Ag^+ and Pb^{2+} are reduced more easily.

Here, we show how a combination of complementary TEM techniques can be used to identify Ba atoms on graphene oxide and to determine their positions with atomic spatial resolution. From their locations, it is in principle then possible to infer the positions of the oxygenated functional groups to which they are attached. It is also of interest to examine how the distributions of the functional groups change with increasing temperature, as the more weakly bound functional groups should then be lost, together with any Ba atoms that are attached to them, allowing the functional groups to be identified. For this reason, we used a highly stable single tilt specimen holder based on microelectromechanical systems (MEMS) technology (DENSolutions, Delft, The Netherlands), which allows specimens to be heated in situ in the TEM to temperatures of up to 1000 °C with no significant loss of spatial resolution and negligible specimen drift. While contamination of the specimen by adsorbed hydrocarbons was always a problem during the examination of GO using STEM imaging and spectroscopy at room temperature, it was discovered during heating experiments that contamination was completely eliminated above a specimen temperature of 400 °C, allowing STEM spectrum images to be acquired over periods of ~15 mins. It is not clear why such high temperatures were required to completely eliminate contamination. Only a small region near the centre of the specimen is heated, so one possibility is that significant hydrocarbons can still migrate from the lower temperature region surrounding the heated area. Without the elimination of contamination by heating the specimen, the experiments that are described below would not have been possible.

2. Experimental details

GO was synthesised from graphite flakes (Sigma-Aldrich) by using an improved method developed by Marcano et al. [25].

Briefly, 9.0 g of KMnO_4 was added to a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (180:20 mL) while stirring. Then, 1.5 g of graphite flakes was added to form a uniform suspension, which was further stirred and heated to 50 °C for 12 h. The reaction mixture was cooled to 5 °C and poured onto ice (200 mL) with 30% H_2O_2 (1.5 mL). The filtrate was centrifuged at 3000 rpm for 1 h and the remaining yellow solid was washed in succession using a 30% HCl solution several times and three portions of water-free ethanol (100 mL). The resulting solid was further washed with Type I water (18 M Ω -cm, ELGA, Purelab Classic) and put into a 10% solution of the trisodium salt of ethylenediaminetetraacetic acid (EDTA) at a pH of ~8 to remove the divalent ions. The mixture was then dialysed against an aqueous solution of HCl (0.05 M) for 24 h and dialysed (Viking C65, diameter 6.5 cm, cut-off 6000–8000 Da) against Type I water for 72 h. The purified solid was added to a solution of BaCl_2 (0.01 M, pH ~11), stirred for 24 h and dialysed against Type I water for 72 h, with water changes twice per day to remove residual non-bonded ions.

TEM specimens were prepared by diluting the solution with Type I water and then dropping it onto silicon nitride membrane chips that were designed for a MEMS-based heating specimen holder. The membranes each contained a number of holes, across which the GO sheets could be suspended. All experiments were carried out using an FEI Titan 60–300 “Pico” microscope equipped with a probe C_5 corrector, a combined image C_5 and C_c corrector and a Gatan imaging filter (GIF). A low accelerating voltage (80 kV) was always used to minimise electron beam induced damage. The C_c corrector allows energy-loss TEM images to be acquired using large (e.g., > 50 eV) energy-selecting slit widths with no significant loss of spatial resolution. The acquisition of energy-loss images with a spatial resolution of 0.1 nm at 80 kV using a non- C_c -corrected microscope would require the use of a narrow energy-selecting slit, resulting in a very small signal at the energy losses that are of interest here. The image C_5 corrector allows a point resolution of 0.08 nm to be achieved at 80 kV, while the probe C_5 corrector allows the same resolution to be achieved for HAADF STEM images.

3. Experimental results

3.1. TEM of graphene oxide

Fig. 1a shows a low magnification bright-field TEM image of a typical region of the GO specimen acquired at 800 °C. The brighter areas, e.g., at the top of the image, correspond to thinner regions that were identified using electron diffraction to consist of either one or a few C layers that were aligned in the same orientation. Darker areas in the image correspond to regions where the carbon layer folded over onto itself during specimen preparation. The detailed examination presented below was carried out on the thinner regions. The image shown in Fig. 1a was acquired slightly underfocus to increase the contrast from the functional groups, which are likely to produce the mottled contrast that varies spatially on a length scale of a few nm. Samples that were imaged at room temperature were consistently found to contaminate, with the source of contamination determined to be the GO itself, as other samples imaged under similar conditions did not exhibit similar problems. A contaminated area, resulting from earlier STEM examination, is visible just to the right of the centre of Fig. 1a. Fig. 1b shows an HRTEM image of the same specimen acquired a few nm underfocus. The image shows a distribution of dark dots that are each presumed to correspond to Ba atoms (see below). However, very little contrast is visible from the functional groups on the GO surface.

Download English Version:

<https://daneshyari.com/en/article/8038313>

Download Persian Version:

<https://daneshyari.com/article/8038313>

[Daneshyari.com](https://daneshyari.com)