

Revisiting Graphene Oxide Structure via Spatially-Resolved Electron Energy Loss Spectroscopy

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Graphite Oxide is known since 1859 and is derived directly from natural graphite by chemical oxidation. Although the adsorption of oxygen perturbs graphite hexagonal lattice, the layered structure is conserved, with an expansion of the interlayer distance to about the double (0.67 nm). Thanks to the hydrophilic character of the oxidized carbon sheets, liquid exfoliation in water is highly effective in yielding Graphene Oxide (GO) single layers. Much interestingly, chemical and thermal treatments allow to lower the oxygen content in GO producing a new material, known as Reduced Graphene Oxide (RGO). GO is eligible for numerous applications including composite materials, molecular sensors, optoelectronic devices, energy storage, photovoltaics and nano-biology. Lately it has attracted a renewed attention as a precursor for a low-cost large-scale production of graphene. Indeed RGO constitutes a valuable form of chemically modified graphene (CMG), since graphene sp^2 symmetry and electronic properties can be retrieved on a good extent. RGO is suitable for applications in electronic devices as flexible and transparent conductor, with the advantage of easy transfer and integration on various substrates.

Certainly, for a highly controlled use of GO and RGO within applications, the knowledge of their atomic structure and hence their electronic properties is fundamental. However, after numerous models have been proposed since the 1940s, the exact structure of these materials is still greatly debated. Its determination is indeed complex, due to GO non-stoichiometric nature, that makes the interpretation of spectroscopic peaks difficult. Moreover, GO varies from sample to sample, because the oxidation method and its related parameters affect the final chemical composition. In the most widely accepted model (Lerf-Klinowski) epoxide and hydroxyl groups are the dominant species and decorate randomly both sides of carbon basal plane, while few carboxylic groups are found at the plane edges. Graphitic aromatic regions and oxidized partially sp^3 hybridized regions are thought to coexist. Spectroscopic studies have evaluated the overall atomic oxygen content in GO in a range from 20% to 35% (respectively 4:1 and 2:1 C/O ratio). Nevertheless GO atomic-scale heterogeneity predicted by the Lerf-Klinowski model requires the use of local analytic techniques. High Resolution Transmission Electron Microscopy (HRTEM) have indeed shown the presence of hexagonally-arranged graphitic areas, extended over 2-3 nm, surrounded by disordered regions whose nature and composition has not been determined. Electron Energy Loss Spectroscopy (EELS) in a Scanning Transmission Electron Microscope (STEM) could in principle provide chemical analysis at the suitable scale, which may represent a substantial breakthrough in the study of GO and RGO.

In this work we investigate GO and RGO thin flakes using core EELS spectroscopy in a STEM microscope. For the study of these materials, this technique has been applied in very few cases,^[1] probably because of their extreme sensitivity to illumination. Covalently bound oxygen atoms are in fact very likely to be mobilized and possibly ejected by a STEM energetic electron beam, as already demonstrated by HRTEM imaging. Illumination damages can be limited by the use of lower accelerated electrons, defocus and shorter acquisition time. However this entails EELS spectra with a very poor S/N ratio, especially considering the inherently weak intensity of EELS signal in the core-electrons energy-loss range. Chemical analysis of GO and RGO becomes thus quite challenging. A new experimental set up has allowed us to overcome these limits: firstly, a liquid nitrogen system at the sample stage, able to cool down the specimen to about 150 K; secondly, a liquid nitrogen cooled CCD camera with a low read-out noise of three counts r.m.s. and a negligible dark count noise. With a 60 keV electron beam and avoiding extra illumination by a fast blanking system,^[2] we have optimized the acquisition parameters. The analysis of specimen evolution under continuous illumination has defined a maximal electron dose of order of $10^3 \text{ e}^- \text{Å}^{-2}$. Finally, the necessary compromise with spectra S/N ratio has imposed a spatial resolution of 3-4 nm.

We have obtained chemical maps of carbon and oxygen atomic contents in few layers GO and RGO. Both materials show evident spatial heterogeneity in the oxidation level on the scale of tens of nanometers. Overall, on the number of analyzed flakes, the oxygen atomic percentage varies from 15% to about 50% in GO and from about 5% to 20% in RGO. Energy-Loss Near-Edge Structures (ELNES) at carbon K-edge in GO can be distinguished in two typical profiles, associated to low and high oxidation levels. In RGO, π^* and σ^* graphitic carbon K-edge ELNES signature, very weak and broad in GO, is extremely intense and sharp. For the interpretation of ELNES carbon K-edge peaks related to carbon-oxygen antibonds, given the difficulty in the

assignment, we propose a new approach combining EELS oxygen quantifications with literature references from X-ray Absorption Near Edge Structure (XANES) studies. It is found that the Lerf-Klinowski model, while compatible with the 20% oxygen GO regions, cannot account for oxygen content such high as about 50% (corresponding to a 1:1 C/O ratio). Considering also the graphitic nature of the material after reduction, we expect that the dominant oxygen group in GO highly oxidized regions is hydroxyl, with an almost full functionalization of the carbon network. On these basis we have associated the more intense carbon-oxygen ELNES structure in GO and RGO to hydroxyl.

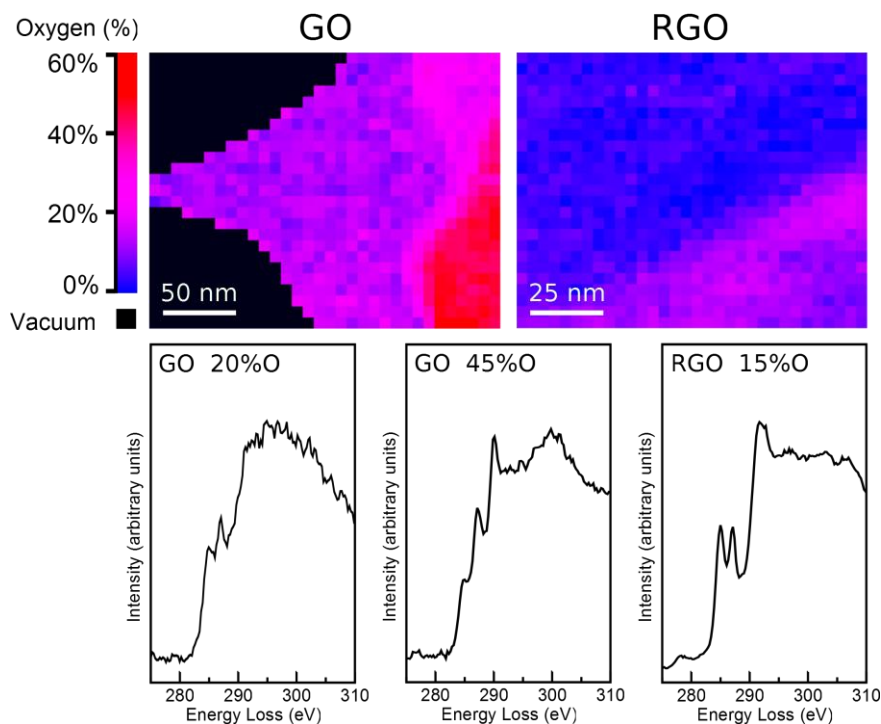


Figure 1. Atomic oxygen maps of GO and RGO thin regions (upper panel) and C-K edge ELNES structures for specific oxidation levels in GO and RGO (lower panel).

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