



## Preparation of graphene oxide and characterisation using electron spectroscopy



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### ABSTRACT

Graphene oxide was prepared from commercial graphene powder (G) platelets of 8 nm thickness by oxidation in ozone (G-O3) and low-energy (cold) glow air plasma in a pink region (G-PP). X-ray photoelectron spectroscopy (XPS) was applied for chemical characterisation of the atomic content and for obtaining quantitative information on C hybridisation. Reflection electron energy loss spectroscopy (REELS) was used for characterising the surface structure including the content of surface and bulk carbon atoms of sp<sup>2</sup> and sp<sup>3</sup> hybridisation.

The G-O3 and G-PP graphene oxide samples contain a low amount of C sp<sup>3</sup> bonds and carbon–oxygen groups in comparison to graphene oxide prepared by the “wet” chemical methods. Oxidation of commercial graphene platelets powder, especially in air plasma, leads to increasing surface C sp<sup>3</sup> and significantly bulk C sp<sup>3</sup> contributions, indicating intercalation by oxygen groups. The intensity ratio of the REELS  $\pi + \sigma$  C sp<sup>2</sup> bulk to the C sp<sup>2</sup> surface energy loss peaks, decreasing in the order G>G-O3>G-PP, indicates exfoliation of layers in G-O3 and G-PP by oxygen functional groups and water with decreasing average number of layers in graphene oxide nanostructures due to oxidation. Although, the “wet” chemical methods are more effective for oxidation leading to a larger amount of C sp<sup>3</sup> and oxygen groups, the proposed methods of oxidation by ozonation and in air plasma are inexpensive, safe, effective, environmentally friendly and do not result in toxic chemical waste products.

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## 1. Introduction

Due to the wide range of physicochemical properties of graphene and the possibility of tailoring these properties using different chemical treatments, graphene research has become an important field for the scientific and industrial community. Elaboration of preparation technology of high quality graphene on a large scale is important. Different forms of graphene have already been prepared using: (i) the adhesive tape-exfoliation of graphite [1], (ii) chemical vapour deposition (CVD) growth [2], (iii) unzipping of carbon nanotubes [3], (iv) other methods based on the exfoliation of graphite oxide [4] and (v) the “wet” methods involving different chemicals (fuming HNO<sub>3</sub>, KClO<sub>3</sub>, NaClO<sub>3</sub>, NaNO<sub>3</sub> and KMnO<sub>4</sub>) like the methods by Brodies [5], Staudenmaier [6], Hofmann [7], Hummers and Offeman [8]. These “wet” methods consist of solution-based preparation of graphite oxide, which is treated usually as a precursor for its further exfoliation to graphene oxide.

The “wet” methods of graphene oxide preparation lead to high content of C sp<sup>3</sup> hybridisations, which can be removed during the reduction process leading to structurally different reduced graphene oxide, as well as to toxic environmentally unfriendly by-products. Therefore, the elaboration of inexpensive and safe methods of synthesis in a gas-phase leading to effective oxidation of graphene platelets is highly demanded.

Chemical and structural investigation of graphene oxide and reduced graphene oxide has been extensively reported using scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infra-red spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS) and reflection electron energy loss spectroscopy (REELS) [1–18]. Characterisation by XPS reveals the surface content of contamination (oxygen, etc.) and the content and nature of carbon bonds attached to oxygen groups (C sp<sup>2</sup>, C sp<sup>3</sup>, C–OH – hydroxyl, C–O–C – epoxy, >C=O – carbonyl, C–OOH – carboxyl, –C(O)OC – ester, etc.) from the intensities and binding energy (BE) values of the C 1s and O 1s spectra. Graphene preparation using the “wet” chemical treatments (the most commonly

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applied method) leads to a large amount of C  $sp^3$  defects and oxygen groups attached to graphene layers [3,11,12,14–17]. Reduction of graphene oxide includes several methods such as thermal reduction and reparative treatment, like CVD repair, chemical treatments using hydrazine, aniline, etc. [9–12]. Graphene oxide prepared by the chemical “wet” methods shows high oxygen content with the content ratio of C/O ranging from 1.12 to 5.0 [9–12,14–17] and the C  $sp^3$  content up to 40% [14], where C  $sp^3$  is formed due to oxygen and possible alkyl groups attachment to carbon atoms. The CVD prepared graphene oxide exhibits lower oxygen content and therefore the higher value of C/O ratio, i.e. 5.7, and lower C  $sp^3$  content [2]. Characterisation of surfaces by the X-ray PhotoElectron Energy Loss Spectroscopy (XP-EELS) and REELS is partially complementary to XPS (describing the content of C  $sp^2$  and C  $sp^3$  hybridisations), however energy loss techniques may also distinguish the information on the solid surface-vacuum interface and the bulk region and reveal the information on the structure. In XP-EELS and REELS the electron passing through a surface layer of a solid interacting with the quasi-free electrons undergoes an inelastic scattering event (causing energy loss) interacting with only  $\pi$  type valence electrons or with  $\pi + \sigma$  type electrons involving all the valence electrons. During the energy loss process charge density oscillations are induced, with plasmons as the energy quanta of the oscillations, where the plasmon energy,  $E_p = \hbar\omega$ , relates to the frequency,  $\omega$ , of the oscillations depending on the density of weakly bond electrons. “Surface excitation”, due to the presence of a solid-vacuum boundary, has a lower frequency than “bulk excitation”, i.e. the energy loss in an infinite medium without any boundary. The experimental values of energy positions of the REELS electron energy loss peaks for graphene [13], graphene oxide [14] and HOPG graphite [18] agree with those obtained from DFT and phenomenological calculations. For HOPG graphite (majority of C  $sp^2$  hybridisations) the REELS  $\pi$  energy loss peak at 6.5 eV and the  $\pi + \sigma$  surface and bulk loss peaks at 19.5 eV and 27 eV, whereas for diamond (majority of C  $sp^3$  hybridisations) the  $\pi + \sigma$  surface and bulk loss peaks at 23 eV and 33.8 eV energy loss were reported [18]. The large free-standing single graphene membranes prepared by micromechanical cleavage of a natural graphite indicated the presence of the C  $sp^2$   $\pi$  and  $\pi + \sigma$  surface plasmon modes in the loss spectra at 4.7 eV and 14.6 eV, in agreement with the theoretical evaluation [13]. With increasing number of graphene layers, the respective excitations for a single, bi-layer and tri-layer graphene increase their values and an additional bulk  $\pi + \sigma$  loss peak at 27.0 eV energy loss is observed for about and/or above 10 layers [13]. The single layer graphene oxide shows the  $\pi$  and  $\pi + \sigma$  surface plasmon modes in the loss spectra at 5.0 eV and from about 15.0–17.5 eV, where the intensity and plasmon energy depends on the type of oxygen groups (hydroxyl, epoxy, carbonyl) and their concentration [14].

In the present work, the graphene oxide prepared from the commercial graphene platelets powder by oxidation in ozone and in low-energy (cold) glow air pink plasma and the similarly treated Highly Oriented Pyrolytic Graphite were chemically and structurally characterised using XPS and REELS analyses.

## 2. Experimental

### 2.1. Samples, preparation and notation

Commercial graphene powder platelets (Graphene Supermarkets, USA) of 8 nm average thickness (producer information) and a Highly Oriented Pyrolytic Graphite layer were placed on Kapton tape and oxidised using two different methods:

1. in ozone  $O_3$  at atmospheric pressure and RT for 5 h,

2. in low-energy (cold) glow air pink plasma [19,20] at the pressure of  $10^{-1}$ – $10^{-2}$  mbar, RT for 5 h, where a cold plasma is generated by electric discharges between electrodes and discharges due to the energy absorption from electric field at the resonance frequency causing molecules ionisation and oxidation. The inductor operated at approximately 15 kV and 27.2 MHz in a pulse, of 1 min on and 1 min off for cooling. The DC voltage supply (Electro-Technic Products, High Voltage Source Model No 1, Chicago, IL USA) operated at 1–2 kV with the current of 1 mA throughout the experiment.

The following sample notation was applied:

- commercial graphene platelets powder – G,
- graphene oxide obtained by sample G oxidation in ozone – G-O3,
- graphene oxide obtained by sample G oxidation in low-energy (cold) glow air pink plasma – G-PP,
- commercial graphene platelets powder bombarded by  $Ar^+$  – G- $Ar^+$ ,
- Highly Oriented Pyrolytic Graphite – HOPG,
- graphite oxide obtained by HOPG oxidation in ozone – HOPG-O3,
- graphite obtained by HOPG oxidation in low-energy (cold) glow air plasma in a pink region – HOPG-PP.

### 2.2. XPS apparatus

The XPS and REELS spectra were measured using the ultra-high-vacuum ESA-31 spectrometer [21] equipped with a hemispherical high energy resolution electron analyser, an electron gun, an X-ray excitation source and  $Ar^+$  ion source. The XPS spectra (survey, narrow C 1s XP-EELS and O 1s) were measured using  $AlK\alpha$  X-rays, in a fixed retarding ratio (FRR) working mode, at photon incidence and electron emission angles of  $70^\circ$  and  $0^\circ$ , respectively, with respect to the surface normal. The REELS spectra were measured using the FRR working mode, a primary electron beam with a spot diameter of 1.5–2.0 mm, a primary electron current of about 5 nA on the sample surface and primary electrons having a kinetic energy (KE) of 4000 eV, electron incidence and emission angles of  $50^\circ$  and  $0^\circ$ , respectively, with respect to the surface normal. Ion sputtering was carried out using an  $Ar^+$  ion beam of energy of 3 keV with a current of  $30 \mu A$  for 1 min on the sample surface.

## 3. Results and discussion

### 3.1. XPS surface chemical characterisation

The survey XPS spectra recorded from the investigated samples are shown in Fig. 1. These spectra show the presence of C, O, and in some cases traces of Si from the glue on Kapton substrate. No traces of other elements are observed contrary to respective samples obtained using oxidising and/or reducing chemical procedures applying sulphuric, nitric acid solutions and for example hydrazine. The surface chemical content of C and O (Table 1) was evaluated from the C 1s and O 1s peak intensities (area) following Tougaard-type inelastic background subtraction [22] and C 1s and O 1s peak area correction for the respective contributions from the substrate, indicating a signal from C, O and Si. Quantitative analysis was

**Table 1**  
Atomic concentrations (%) of C and O at the surface. The sample notation is described in Section 2.1.

Atoms	HOPG	HOPG-O3	HOPG-PP	G	G- $Ar^+$	G-O3	G-PP
O	2.5	4.1	4.8	15.4	1.3	18.4	34.8
C	97.5	95.9	95.2	84.6	98.7	81.6	65.2
Ar	0	0	0	0	3.1	0	0

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