Electron energy-loss spectra of graphene oxide for the determination of oxygen functionalities

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Graphene for large-scale industrial production can be obtained starting from graphene oxide (GO). The structure of GO consists mainly of hydroxyl (-OH) and epoxy (C-O-C) functional groups in the basal planes and carbonyl (C=O) and carboxylic (-COOH) functional groups at the edges of graphene flakes [1]. The presence of oxygen functionalities opens an electron energy gap that can be modulated by modifying the amount of oxygen in the structure and this can be achieved by various reduction methods such as thermal processes, chemical treatments or UV irradiation. In such a way, the electronic properties of GO can be suitably modulated between the insulating and the conductive behavior [2].

Furthermore, while graphene is hydrophobic and graphene flakes tend to precipitate in a water solution, the polar oxygen functional groups of GO render it strongly hydrophilic. Therefore, GO is highly dispersible in many solvents and it can be easily processed for further derivatization and it find application for water purification [3], biomedical technology [4] and microelectronic devices [5].

The composition and the structure of GO and reduced GO (RGO) depend on the synthesis and reduction methodologies. Although several models have been proposed, the composition and the structure of GO and RGO have not yet been clarified. The different strategies of derivatization of GO for subsequent applications can be improved by the identification of the distribution at atomic resolution of the various oxygen functional groups on the GO surface.

For this purpose, we prepared GO by a modified Hummers method and it was reduced by pulsed laser irradiation using visible wavelength (532 nm). Scanning transmission electron microscopy analyses were performed and dual electron energy-loss (EEL) spectra were acquired in different regions of GO and reduced GO flakes by a Jeol ARM 200 equipped with a cold FEG electron gun, CEOS condenser aberration corrector and Gatan "Quantum" EEL spectrometer. The accelerating voltage of the electron beam is 60 keV.

Experimental results show a series of characteristic peaks related to C and O K-edge shells [6]. In particular, the C K-edge shows a multi-peak region situated between 285 and 288 eV with different intensities depending on the analyzed region and a contribution starting at about 292 eV attributable to the $1s\text{-}\pi^*$ and the $1s\text{-}\sigma^*$ electronic transitions, respectively. The experimental EEL signal of the O K-edge spectra presents a peak at about 531 eV and other peaks at higher energies (Fig.1).

In order to better comprehend the core-loss EEL spectra acquired for the C and O K-edges of our GO samples, density functional theory calculations have been performed in order to compute core-loss EEL spectra of graphene oxide (C and O K-edges) with different oxygen functional groups (OH and C-O-C at different concentrations, O in vacancies) by using the WIEN2K full-potential augmented-plane-wave code [7]. EEL spectra were computed with the TELNES3 post-processing program using a Gaussian broadening of 0.5 eV.

The calculated resonance for the π* peak of C K-edge is different for the O-bridge and -OH configurations (287.3 eV and 285.9 eV respectively) from pure graphene (285.2 eV), see Fig.2. Combining only these two configurations (OH or bridge on graphene), the difference in the resonance position gives rise to a double π* peak in the mixed spectrum, the one at 287 eV is predominant at higher concentration of epoxides with respect to hydroxyls groups. Fig.2 shows the experimental and simulated EEL spectra of the 1s-π^* signal of GO.

The simulations of the high-loss EEL spectra at atomic level allow associating the observed experimental peaks to the presence of different oxygen functional groups on the graphene surface and the corresponding atomic configurations (C-OH, C-O-C, O in vacancies), permitting to obtain the mapping of the different functionalities of GO at spatial resolution of the EELS probe (< 1 nm).

References

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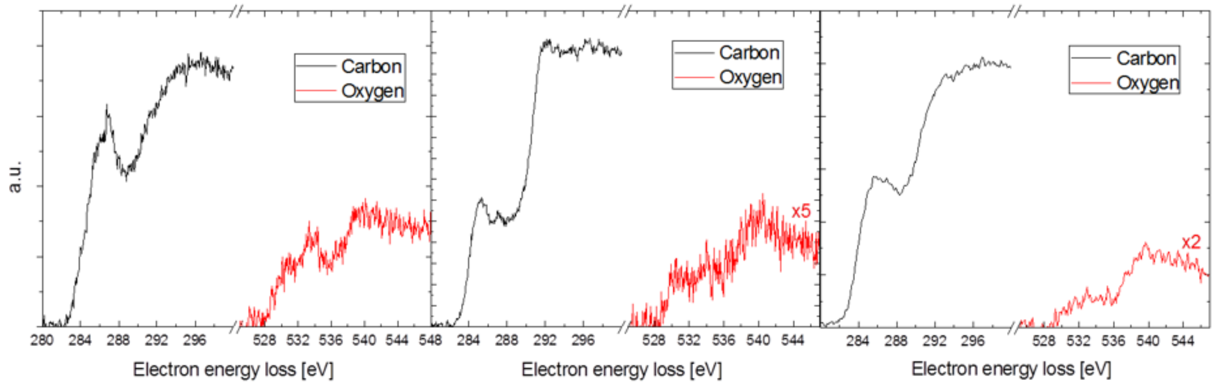

Figure 1 – Dual EEL spectra of the C and O K-edges of three different regions of a GO flake.

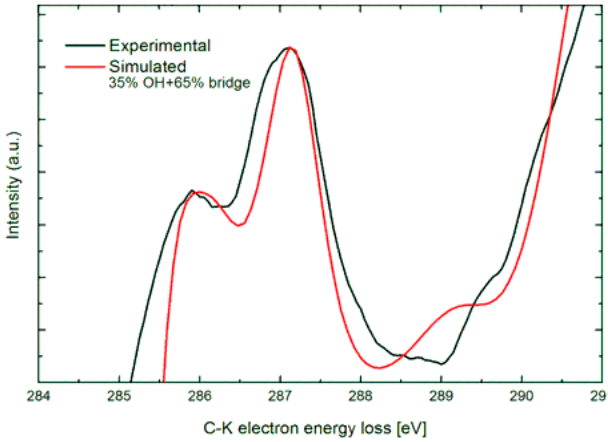

Figure 2 – Experimental (black curve) and simulated (red curve) EEL spectra of the 1s-π^* signal of GO.