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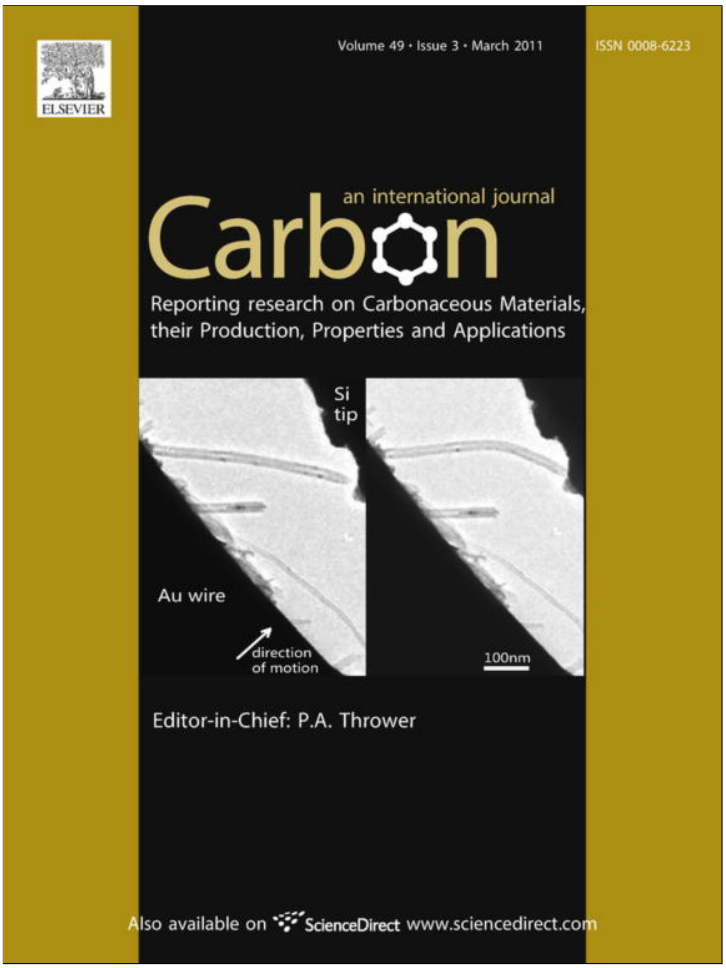

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Electronic properties and atomic structure of graphene oxide membranes

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ABSTRACT

We have performed a near-edge X-ray absorption fine-structure (NEXAFS) and a transmission electron microscopy (TEM) investigation of freely suspended graphene oxide (GO) sheets. We utilized a photoemission electron microscope to identify GO membranes and to acquire C *K* and O *K* absorption spectra. The overall line shape of C K-edge spectra demonstrates that the honeycomb carbon network of graphene is the scaffold of GO. However, the intensity ratio of π^* and σ^* resonances, and a broad feature at about 20 eV from the edge, indicate the presence of new carbon bonds. The O K-edge spectra show that oxidized regions are made of carbonyl, epoxide, and hydroxyl groups attached to the plane of graphene, while carboxyl groups might also be present at the edges. Further, our study indicates the presence of ordered arrangements of oxygen atoms in GO sheets. Our investigation provides a new and efficient route to study the electronic structure of suspended membranes.
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1. Introduction

Graphene oxide (GO) has recently attracted attention as possible precursor in the production of single and few-layers graphene. The intercalation of graphite with strong oxidizers (for instance a mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate, by Hummers method [1]) yields an expanded graphite structure, with double interlayer spacing and oxidized graphene layers. By chemical or thermal treatment, GO layers can be further separated and reduced into graphene sheets with partially recovered electronic properties [2]. Among micromechanical exfoliation of graphite [3], epitaxial growth on silicon carbide [4] and chemical vapor deposition of hydrocarbons on transition metals [5], chemical reduction of GO is the most promising route for a large scale graphene production. Although GO was first prepared in the mid 1800s [6], its composition and structure is still under debate, and several conflicting models have been proposed. The GO sheet is described as either flat (Hofmann [7] and Lerf–Klinowski models [8]) or regularly distorted (Ruess [9], Scholz–Boehm [10], Nakajima–Matsuo [11] and Dékány [12] models), with epoxide and hydroxyl groups attached to carbon atoms in different geometries depending on the model, while the presence of carbonyl species is

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debated. Experimental investigations have also showed controversial aspects of the chemical composition of GO [12–15], only partially justified by different synthesis conditions. The understanding of the physical properties of GO is important in order to improve the reduction process, if GO is used as precursor for a mass production of graphene. Further, GO itself is an exciting material for its possible applications, including ion conductor, protective layer, or material for molecular storage [16].

Aim of the present investigation is to reveal the electronic and structural properties of suspended GO sheets, i.e. in the regime of single and few-layers, by means of spatially resolved near-edge X-ray absorption fine-structure (NEXAFS) and transmission electron microscopy (TEM) investigations. We show that GO membranes are prevalently made of separated phases, i.e. clean graphene regions and oxidized ones alternating on a few-nm scale. The chemical composition of oxidized patches is revealed by our NEXAFS investigation. Previous NEXAFS studies described the electronic structure and chemical composition of bulk graphite oxide [17] and of electrophoretically deposited graphene oxide and graphene films [18]. Specifically, polarized NEXAFS measurements of GO films [18] enabled identification of surface functional groups and provided useful insight on the orientation of the graphene sheets. Here we acquired for the first time polarized and spatially resolved NEXAFS spectra on ultra-thin free-standing GO membranes, providing well structured O *K* edges spectra that allow the identification of functional groups and the characterization of the intrinsic electronic structure of GO.

2. Experimental

Graphite oxide was prepared starting from graphite flakes according to Hummers method [1]. The resulting powder was dispersed in water by mild sonication. Such obtained GO sheets were deposited on Quantifoil(R) TEM grids with 1.3 μm holes by dipping the grids into the solution for 8–10 min and drying with nitrogen gas. After this preparation, we find single- and few-layer graphene oxide membranes freely suspended across some of the holes in the grids, as verified by TEM imaging and electron diffraction. The TEM images were obtained using an image-side aberration-corrected Titan 80–300 (FEI, Netherlands), operated at 80 kV. The spherical aberration was set to 20 μm and the atomically resolved image (Fig. 1d) was recorded at Scherzer defocus (ca. −90 nm).

The laterally resolved NEXAFS experiments were performed at the surface/interface:microscopy (SIM) beamline of the Swiss Light Source, using an Elmitec PEEM equipped with an energy analyzer. Element-specific PEEM contrast was obtained by dividing pairs of images recorded at the absorption edge and below the edge, thus reducing topographic effects and enhancing the chemical contrast. NEXAFS measurements were obtained by processing stacks of PEEM images obtained by scanning the incident photon energy across C *K* and O *K* edges. The measured total electron yield (TEY) of the region of interest was then normalized to the TEY collected from an external area. Measurements were performed at grazing incidence (16°) with respect to the plane of the grid, with the linear polarization vector nearly-

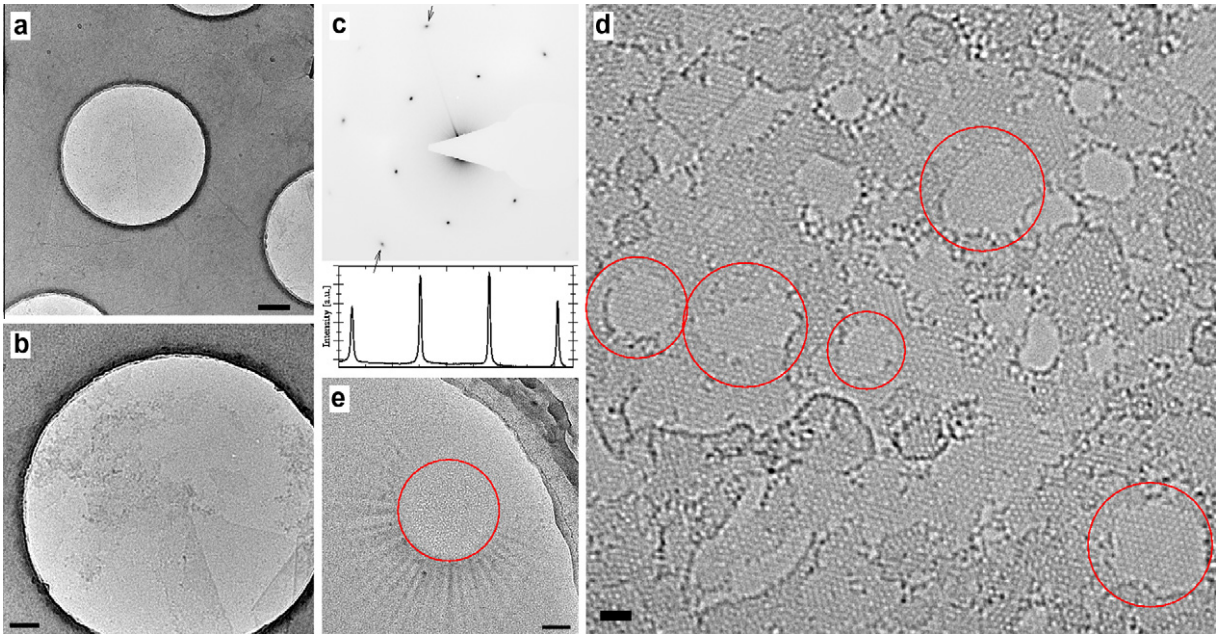

Fig. 1 – TEM analysis of the GO sample. (a and b) Overview images showing representative holes in the Quantifoil TEM grid covered by graphene oxide membranes. (c) Electron diffraction pattern for a single-layer region, and a line profile as indicated by arrows. The outermost spots correspond to the 1.23 Å (1–210 type) reflections. (d) Atomically resolved image from a single-layer region (unfiltered single exposure). Patches of clean graphene are visible (circles) but most of the area is covered by adsorbates or functional groups. (e) Effect of electron irradiation on graphene oxide: after strong exposure of the central area (circle, exposed for high-resolution imaging), distortions in the surrounding membrane indicate a shrinking of the central area under the beam. Scale bars are (a) 200 nm, (b) 100 nm, (d) 1 nm, and (e) 50 nm.

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perpendicular ($\mathbf{E} = \mathbf{E}_1$) or parallel to the grid ($\mathbf{E} = \mathbf{E}_2$). The two configurations enhance transitions into final states of π or σ symmetry of graphene, respectively. The NEXAFS spectra here reported are recorded on microscopic regions of free-standing GO membranes with no contribution from the support grid. To improve the statistics, the average spectrum of several GO regions is reported.

3. Results and discussion

We begin our discussion with the TEM results in Fig. 1. Lower magnification TEM imaging and electron diffraction confirms the successful preparation, i.e. a coverage of ca. 10% of the holes in the Quantifoil TEM grids with single- and few-layer graphene oxide membranes (Fig. 1a–c). Fig. 1d shows an atomically resolved exposure of single-layer GO. With the present setting of spherical aberration and defocus, dark contrast in this image can be directly interpreted in terms of atomic structure. This image (and many similar ones) show small patches of clean, defect free graphene (indicated by circles), while most of the area is covered by adsorbates or functional groups with no obvious structure. The TEM images confirm that GO membranes consist of ordered (graphene-like) segments along with functionalized areas that alternate on a few-nm scale, in agreement with previous models [12,19] and experimental studies [21,22].

For the analysis of the functional groups in GO by high-resolution TEM imaging, several complications should be noted: first, the atomic contrast of carbon, nitrogen and oxygen is nearly identical, such that their distinction within the adsorbates is difficult. Second, graphene sheets prepared under ambient conditions frequently contain "contamination" carbonaceous adsorbates, which are difficult to distinguish from functional groups (this complication was also noted by Wilson et al. [22]). Baking to high temperatures is usually employed to remove such contamination, but in the case of GO, already mild baking leads to reduced GO [20], i.e. it also removes the functional groups. Third, GO membranes are visibly affected by the TEM electron beam. For example, Fig. 1e shows a larger area of a GO membrane after exposing the central region for high-resolution imaging (dose within the red circle was ca. $10^8\ e^-/\mathrm{nm}^2$): radial wrinkles have appeared in the surrounding membrane, outside of the strongly exposed central area. This indicates a significant shrinking of the strongly exposed area under the beam. In our interpretation, the wrinkles form as the surrounding membrane complies with a shrinking of the central area. In any case, the effect indicates that TEM images of this material may not represent the original structure of GO.

We note that the structure of *reduced* graphene oxide (RGO), i.e. the defects that remain after removing the functional groups, was successfully unraveled by aberration-corrected TEM using the same conditions [23]. In this case, the samples can be baked to reduce contamination, are stable under the beam, and are made of mostly carbon. In the comparison, our TEM images from GO show much stronger coverage with adsorbates (functional groups or contamination), and do not display the extended topological defects that are frequently seen in the RGO samples [23]. In the following discussion, we analyze the functional groups of GO from their NEXAFS spectra. In contrast to previous studies [17,18], these were recorded on ultra-thin free-standing membranes, reducing potential effects of substrate interaction or bulk agglomeration.

Fig. 2 shows PEEM images collected at the C *K* edge (a) and O *K* edge (b), for a total exposure time of about 30 s. Dashed lines were superimposed on images to identify some of the suspended GO membranes. The contrast provided by the PEEM demonstrates that the concentration of carbon atoms is higher than that of oxygen atoms (an average ratio of about 5:1, as calculated from integrated intensities of NEXAFS spectra), and each small region suspended across a single hole (1.3 μm of diameter) can be composed of a different number of layers. For instance, arrow *a* of Fig. 2a points out one of the thinnest areas seen by the PEEM, thus assumed to be a single-layer region. Our TEM analysis indicates that the maximum number of layers is below ten, corresponding to the brightest areas in our PEEM images (arrow *b*). Fig. 2b shows that the density of oxygen atoms is not uniformly distributed

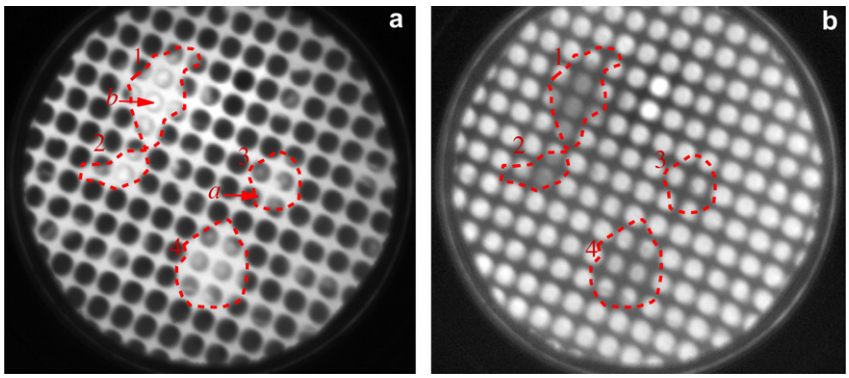

Fig. 2 – PEEM images taken at the C *K* edge (a), and O *K* edge (b), of thin GO membranes. Holes of the grid are 1.3 μm. Dashed lines are guide to the eye, indicating different GO membranes on the TEM grid. In Fig. 2b, overall absorption intensity is significantly higher inside the holes of the grid than in GO membranes, indicating signature of oxygen in the substrate used to mount the grid.

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over the membranes. The upper-left membranes (number 1 and 2) show a lower density of oxygen atoms, while membrane number 3 is barely distinguishable from an empty hole. A precise determination of the number of GO layers on the basis of the PEEM contrast is here difficult, due to the small size of GO membranes and to the absence of a clear border between areas of different thickness. Nevertheless, our PEEM results reveal the electronic structure of GO in the few-layers regime.

In Fig. 3a, we show NEXAFS measurements recorded across the C *K* edge of GO membranes, using the nearly-perpendicular photon polarization vector $\mathbf{E}_1$. We compare the NEXAFS spectrum (thin line) of a single-layer region (indicated by arrow *a* in Fig. 2a) with an average spectrum (bold line) obtained from several regions from selected membranes (1–4) that span the holes in the support film, with a different number of layers. The inset of Fig. 3a shows the C *K*-edge spectrum of a single-layer graphene membrane freely suspended across the hole of a Quantifoil(R) TEM grid, taken by using $\mathbf{E} = \mathbf{E}_1$. The line shape of this spectrum is the one reported for single-layer graphene on SiO_2 substrates [24,25]. Due to the polarization of the light, the absorption spectrum of graphene is dominated by the first resonance (π^*) at 285.5 eV, while, above the first σ^* resonance, high energy features are suppressed. This peculiarity of the NEXAFS spectrum of graphene [24] can be explained by the multiple-scattering theory, namely considering the scattering of the excited electron wave function by neighboring atoms. Due to an open *cage* around the absorbing atom when the polarization of the light would select atoms above and below the graphene plane, high energy features of the C *K* edge spectrum are suppressed. NEXAFS spectra of graphene and few-layers graphene [24] showed that high energy features of the C *K* edge spectrum are fully recovered above 5 layers. Interestingly, regardless of the number of layers, the same behavior is found here for GO membranes. Above 310 eV, the NEXAFS spectrum of GO is almost featureless, reflecting the much higher interlayer distance (typically 0.6–0.7 nm [8,12,26]) of GO compared to that of graphite (0.34 nm). This finding shows that the electronic structure of GO is largely insensitive to the number of layers, as expected for a material composed of strongly decoupled layers. We point out that the overall line shape of the absorption spectrum of GO (Fig. 3a) reflects the sp^2 hybridization of carbon atoms. Nevertheless,

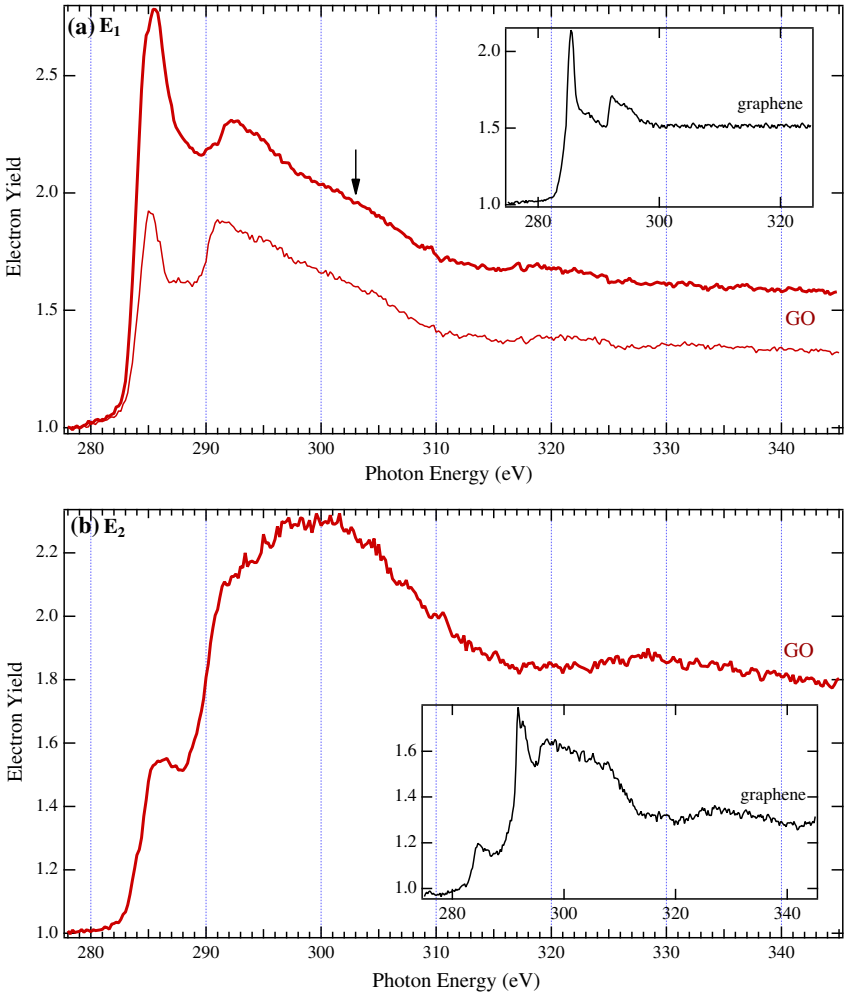

Fig. 3 – C *K*-edge absorption spectra of single-layer GO (thin line) and average few-layers (thick line) taken with a linear polarization vector: (a) nearly-perpendicular to the plane of the grid (E_1); (b) parallel to the plane of the grid (E_2). In the insets corresponding spectra, taken at E_1 and E_2, of a freely suspended single-layer graphene membrane are reported.

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with respect to the NEXAFS spectrum of graphene, interesting differences are found. The ratio between the π^* and first σ^* resonance (at about 292 eV) is reduced in the absorption spectrum of GO, indicating a new component of carbon atoms with sp^3 hybridization. This ratio can be locally different in our samples, as seen comparing the average spectrum (bold line) of Fig. 3a with the one of a single layer (thin line), where a reduced total intensity of emitted electrons is also found, due to a lower number of absorbing atoms. Changes of the π^*/σ^* ratio in our GO membranes indicate a locally different degree of oxidation, as confirmed by the PEEM contrast at the O *K* edge (Fig. 2b). Interestingly, the NEXAFS spectrum of Fig. 3a shows a broad hump at about 303 eV. This peak corresponds to C=C σ^* convoluted with C=O σ^* resonances [27], demonstrating the presence of double bonds in the honeycomb carbon network, and of carbonyl groups. Finally, a broadening of the π^* exciton peak, from 1.0 eV in the spectrum of graphene (inset Fig. 3a) to 2.2 eV (Fig. 3a), confirms that the local order is reduced.

In Fig. 3b corresponding spectra of GO (average spectrum) and graphene (inset) are shown for the photon polarization vector $\mathbf{E}_2$. The NEXAFS spectrum of graphene exhibits a non vanishing π^* peak, due to possible misalignments of the suspended flake with respect to the support grid, and a strong on-set of the σ^* transition at 291.8 eV, with clear excitonic character [28]. Going from graphene to GO (Fig. 3b) the excitonic peak disappears, reflecting the existence of defects and lower order in the structure of GO. The broadening of the π^* resonance reflects both a lowering of the local order in GO and a density of states composed by multiple-peaks in the few-layers regime [24]. Moreover, a lowering of the π^*/σ^* ratio indicates a component of carbon atoms with sp^3 hybridization, as clearly evident from Fig. 3a also. The origin of this component is revealed by the O *K* edge spectra (Fig. 4), recorded with $\mathbf{E} = \mathbf{E}_1$ (a) and $\mathbf{E} = \mathbf{E}_2$ (b). Spectra of Fig. 4 were also extracted from the four selected membranes (Fig. 2b) and reported as average. Comparing regions with different oxidation level mainly gives O *K* edge spectra with different integrated intensities. Peak *a* at 531.5 eV is assigned to the π^* state of C=O, which may belong to carbonyl groups bonded to an aromatic ring [29], and likely to COOH groups attached at the graphene oxide edge sites [17,18]. Peaks *e* and *f*,

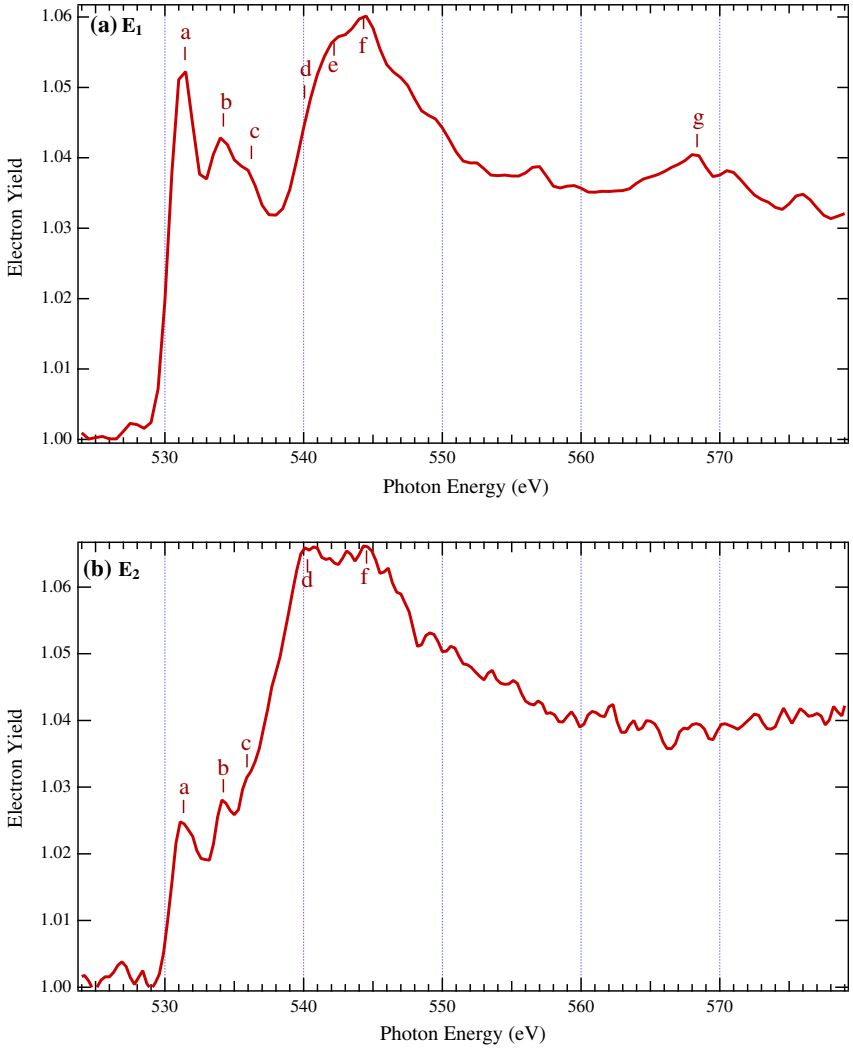

Fig. 4 – O *K*-edge absorption spectra of average few-layers GO taken with a linear polarization vector: (a) nearly-perpendicular to the plane of the grid (E_1); (b) parallel to the plane of the grid (E_2).

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Table 1 – Excitation energies and assignment in O K-edge absorption spectra of GO membranes.

Peak	Energy (eV)	Assignment	Refs.
a	531.5	π^*(C=O)	[17,18,29]
b	534.0	π^*(C–O)	[17]
c	535.5	σ^*(O–H)	[29,30]
d	540.0	σ^*(C–O)	[18,29]
e	542.0	σ^*(C=O)	[29]
f	544.5	σ^*(C=O)	[29]

at 542.0 eV and 544.5 eV, respectively, are σ^* resonances related carbonyl groups also [29]. This finding demonstrates that C=O species directly bonded to aromatic rings of graphene do exist in the basal plane of GO, as previously argued by the line shape analysis of the C1s photoemission peak of GO [12]. Peak *b* at about 534 eV can be related to the π^* state of C–O from epoxide [17], while peak *c* at 535.5 eV is a fingerprint of OH groups [29,30]. Summary of the assignment of the peaks for the O *K*-edge spectra is shown in Table 1.

Going from a photon polarization vector almost perpendicular to the grid ($\mathbf{E}_1$) into a parallel one ($\mathbf{E}_2$), the broad peak centered at about 542 eV dominates the spectrum. In this configuration, the *d* peak at about 540 eV, assigned to C–O σ^* states derived from basal phenolic groups [29,18], become more intense, while the *g* peak at about 568 eV (Fig. 4a) disappears. This high energy feature can be related, in a multiple-scattering theory approach, to the interference occurring between the forward-propagating emitted wave and the wave backscattered from the surrounding shells of atoms. The fine structure of the oxygen edge spectra reported in Fig. 4 exhibits remarkably sharp, distinct features, affected by the polarization of the light, suggesting a locally ordered arrangement of oxygen atoms [31]. This is in contrast to a previous TEM study where an amorphous structure of oxygen atoms was concluded [13] (we note again that the functional groups are quickly affected by the electron beam, and that the presence of amorphous contamination complicates the interpretation of TEM results). Nevertheless, on the basis of our NEXAFS investigation we conclude a local order of oxygen atoms in our GO membranes. Considering that the intensity of peak *a* is strongly reduced going from $\mathbf{E}_1$ to $\mathbf{E}_2$ in Fig. 4a and b, this indicates that on the average carbonyl species are oriented along the graphene plane, as described by both the Scholz–Boehm [10] and Dékány models [12].

4. Conclusions

Our TEM and NEXAFS results demonstrate that the structure of GO membranes prepared by Hummers method is prevalently made of carbon atoms with sp^2 hybridization. TEM measurements show that oxidized patches exist along with clean regions of graphene, and the thickness of GO membranes ranges from a single to few-layers (below 10). Our C *K*-edge spectra provide a clear fingerprint of a dominant sp^2 hybridization of carbon atoms, and demonstrate that the coupling between layers is strongly reduced with respect to the one of graphite, while defects and attached groups are also present. Our O *K*-edge spectra clarify the chemical composition of oxidized patches, showing carbonyl groups, together with epoxide and hydroxyl groups, attached to aromatic rings, and carboxyl groups likely attached to the edges of the membranes.

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