

Unravelling the structure-property relationship in Graphene Oxide at low degree of oxidation.

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Supporting Information Placeholder

ABSTRACT: Graphene oxide (GO) is a versatile 2D material, whose properties can, in principle, be tuned by changing the type and concentration of oxygen containing functional groups attached to its surface. However, a detailed knowledge of the dependence of the chemo/physical features of this material on its chemical composition is largely unknown. In this paper, we combine classical molecular dynamics (MD) and density functional theory (DFT) simulations to predict the structural and electronic properties of a large collection of GO samples at low degree of oxidation and suggest a revision of the widely accepted Lerf-Klinowski structural model. We find that layer deformation is larger for samples containing high concentrations of epoxy groups and that correspondingly the band gap increases. Targeted chemical modification of the GO surface appears to be an effective route to tailor the electronic properties of the monolayer for given applications. Interestingly our simulations also show that an analysis of the chemical shift of the *C-1s* XPS peak allows one to unambiguously characterize GO composition, resolving the peak attribution ambiguities often encountered in experiments.

Graphite oxide was first synthesised by Brodie in 1859¹, treating graphite with a solution of strongly oxidising acids. Graphite then exfoliated into a suspension of Graphene Oxide (GO) flakes. These flakes can be as thin as one atomic layer, like graphene. There exist several models² which have been proposed to describe the structure of GO. The Lerf-Klinowski model³ is one of the most widely accepted for moderately oxidised samples, and it has been recently validated by NMR studies². This model describes GO as a corrugated network of sp^2 -hybridised carbon regions and randomly distributed sp^3 domains with epoxides and hydroxyls mostly adsorbed at the graphene basal plane with carbonyl and carboxyl groups at the edges of the flakes. The oxidation

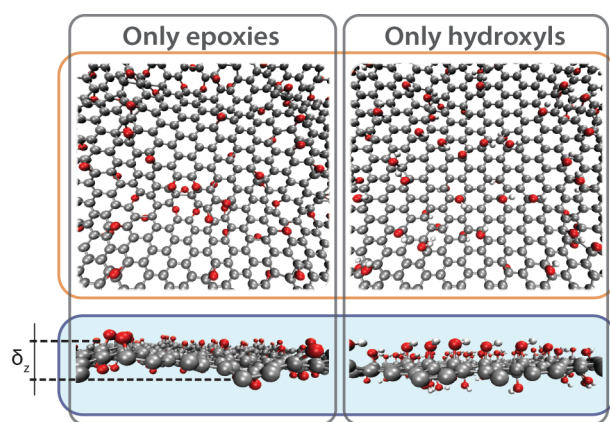


Figure 1. Ball and stick representation (side view in light blue panel, with definition of vertical displacement δ_z) of two GO structures at 20% degree of oxidation: a sample with only epoxy (-O-) (left side) and one with only hydroxyl (-OH) groups (right side).

level and type of adsorbed functional groups vary significantly and can be controlled by varying the reduction processes⁴.

GO has been studied in a large number of works, both experimentally⁵⁻⁹ and theoretically¹⁰⁻¹³, and several applications are currently under consideration¹⁴. For example, GO has been proposed as an option for graphene mass production¹⁵, exploiting the reduction of oxygen-containing species and subsequent healing of the introduced defects¹⁶. Indeed, while the direct production of graphene requires complex and time expensive techniques, such as mechanical exfoliation¹⁷, chemical vapour deposition or epitaxial growth¹⁸, GO can be obtained via simple chemical processes, which imply lower costs and time of production. GO has also attracted a great deal of interest due to its peculiar electronic properties: among various applications, GO has been proposed as hole injection layer for MoS₂-based electronic devices¹⁹, as an electrode material for rechargeable met-

al-ion batteries²⁰ or to realise GO/graphene vertical heterostructures for highly efficient and flexible organic light emitting diodes²¹.

The electronic properties of GO strongly depend on its preparation and treatment conditions. Recent experiments have shown that GO undergoes a transformation from insulator (highly oxidised, as produced, samples) to semiconductor and even semimetal upon reduction⁴. In this regard, it would be desirable to engineer GO physical properties for targeted applications by knowing precisely how these depend both on changes in oxygen content and on the type of adsorbed functional groups. Experimentally, typical semi-quantitative analysis of GO chemistry is usually achieved through X-ray photoelectron spectroscopy (XPS). Although a detailed deconvolution of the different contributions to the carbon *1s* photoelectron peak could, in principle, be used to determine the nature and concentration of functional groups present in GO, the assignment of the chemical shift has been controversial. Several studies have reported distinct positions for the *C-1s* signal when bonded to hydroxyl or epoxide groups^{5,6,22}, while in some cases the same chemical shift is assigned to both groups^{7,23}. On the theoretical side, first principle calculations have been employed to show how the presence of oxygen containing groups affects the electronic structure of graphene opening a band gap in GO¹⁰⁻¹², but these studies are restricted to small supercells, with symmetrically adsorbed functional groups, which do not grasp the amorphous nature of GO and the great variability of possible structure and configurations of real samples.

The aim of this study is to predict by means of *ab initio* calculations the structural and electronic properties of GO as a function of the degree of oxidation and of the relative concentration of the most abundant functional groups experimentally observed on the GO basal plane, namely hydroxyl (-OH) and epoxide (-O-) species²⁴. Our results reveal in detail how the structural deformations and electronic properties depend on the kind of oxygen-containing species and their concentration. Atomistic simulations also reveal the presence of 1,2-ether groups within the GO structure, which, despite their significant effect upon the properties of GO, to our knowledge has not been reported in literature until now. 1,2-ethers have previously been reported only at the edges of GO structures or around holes in the basal plane^{25,34}. Finally, it is shown that simulated XPS spectra provide an unambiguous assignment of each functional group to the chemical shift of the *C-1s* signal.

Realistic GO samples were obtained using a combination of classical MD and all-electrons hybrid B3LYP-DFT simulations, as reported in details in the Supporting Information. Starting from rectangular supercell structures with randomly distributed -O- and -OH groups (two examples are shown in Figure 1), we first performed a classical MD thermal annealing at room tem

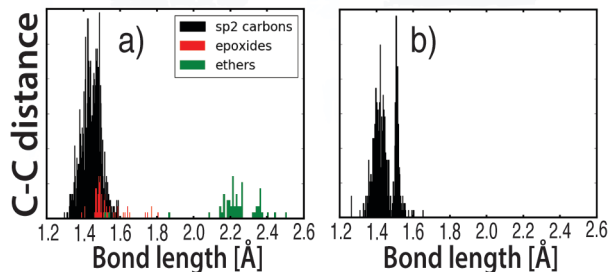


Figure 2. C-C bond length distribution for GO samples at 20% oxygen coverage with only epoxide groups (a) and only hydroxyl groups (b).

perature and constant pressure using a reactive force field²⁶. A final step of DFT optimisation followed²⁷ and results on the structural and electronic properties analysed. XPS spectra were obtained by computing the eigenvalues relative to the core electrons of carbon atoms. This approach has the undoubted advantage of reducing significantly the computational expense with respect to many-body (e.g. GW-BSE) or Δ -SCF techniques, allowing the investigation of a much larger set of configurations.

We studied GO samples at 10% and 20% degree of oxidation (atomic coverage $\Theta = 10\%$ and 20%) and variable ratios between -OH and -O- groups (-OH/-O- = 0%, 25%, 50% and 100%). The chosen coverages, Θ , correspond to the ones usually reported for GO at low degrees of oxidation, according to experimental literature^{4,7}. To make statistically relevant analysis, for each degree of oxidation and -OH/-O- ratio, we generated six independent GO samples and made an unweighted average of the results. Structural characterization was achieved by calculating, for all samples, the distribution of the C-C distance (d_{CC}), which is indicative of in-plane deformations, and the average out-of-plane displacement ($\overline{\delta_z}$), which represents the structural corrugation of the graphitic plane. As reference, the simulated pristine graphene has a flat structure ($\overline{\delta_z} = 0$ Å), where the calculated equilibrium C-C bonds are 1.42 Å, in agreement with that observed in experiments²⁸ and with previous B3LYP simulations²⁹. When only -O- groups are present in the initial GO structure, the C-C distribution shows three peaks (see Figure 2a for samples with $\Theta=20\%$). The black peaks in Figure 2a between 1.3 Å and 1.5 Å correspond to distorted graphene-like C-C bonds, while the red peaks between 1.4 Å and 1.8 Å are due to C-C bonds bridged with epoxide oxygens that change the hybridisation of the carbon atoms to sp^3 and induce an increase in the C-C graphitic bond length. Concerning the green peaks between 2.1 Å and 2.5 Å, these can be assigned to broken C-C bonds originated by 1,2-ether groups within the layer basal plane. Bond breaking has been confirmed by performing Bader topological analysis³⁰, as described in detail in Supporting

Information, which allows one to uniquely determine the presence/absence of a covalent bond. We note that for samples at a lower degree of oxidation the ratio of epoxide/ether groups increases. We observed that ethers are preferably formed when several $-O-$ groups are clustered around the same aromatic graphene ring, or in its immediate vicinity. Figure 2b represents the C-C bond length distribution when only hydroxyl groups at $\Theta=20\%$ are present in the samples. The main effect of $-OH$ adsorption is to change the hybridisation of the carbon atom to which it is bonded from sp^2 to sp^3 . The bond lengths of these carbon atoms with their neighbours (d_{CC}) increases to ~ 1.5 Å as in sp^3 hybridisation, shown by the tallest peaks between 1.5 Å and 1.6 Å in Figure 2b. No broken C-C bonds are observed in this case. Concerning the average corrugation of the samples, as a general trend, we observed that the corrugation increases as the degree of oxidation increases: for a given oxygen content, δ_z is larger for samples containing more epoxy/ether groups than $-OH$ (see Supporting Information for further details).

Oxidation extent has a profound effect also on the electronic properties of GO as evidenced by an analysis of the electronic density of states (DOS) in the region of the valence and conduction bands. As shown in Figure 3, if only epoxide/ether groups are present the average energy gap between valence and conduction bands is about 0.8 eV; this value reduces to roughly 0.6 eV when epoxides/ethers coverage corresponds to $\Theta=10\%$ ³¹. Hydroxyl groups give rise to sharp defect states (peaks) at the Fermi level, which are responsible for metallic behaviour of the samples. This trend can be understood by studying the adsorption of $-OH$ groups at low coverage (see Supporting Information). In particular it is shown that the adsorption of $-OH$ groups on graphene breaks the symmetry of $\pi - \pi$ bonds, causing electrons to localise in states occurring at the Fermi level. In general, when several $-OH$ groups are present in GO the specific effects on the electronic properties depend on the relative positions of the $-OH$ groups in the layer, which is intrinsically amorphous. The effect is to induce high density states in proximity of the Fermi level, yielding structures with metallic behaviour. The effect of $-OH$ groups, on the overall DOS of the samples, prevails in the case of mixed structure, inducing states in correspondence with the Fermi level.

The above results demonstrate that being able to quantitatively determine the relative amount of $-OH$ and $-O-$ functional groups in GO is of paramount importance to engineer its structural and physical properties for selected applications. XPS chemical shift are often employed for this purpose but, as previously stated, peak attribution is not easy to achieve experimentally. In this respect, an analysis of the core level energies, calculated at DFT level, can give a fundamental contribution. Analysing the core level energies of each carbon atom

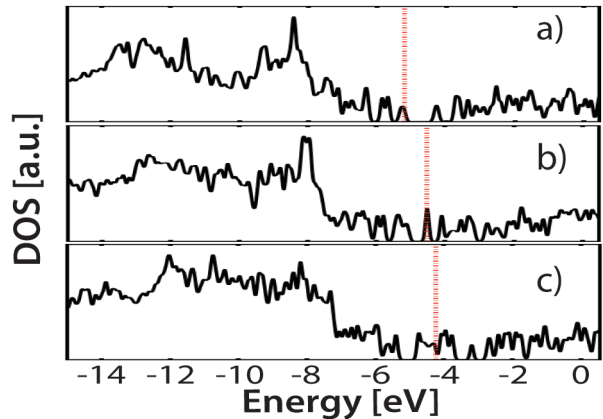


Figure 3. DOS of GO at $\Theta=20\%$ oxygen coverage with only epoxide/ether groups (a), with 50% of epoxide/ether and 50% of hydroxyl groups (b) and with only hydroxyl groups (c). The dotted line corresponds to the last occupied state.

contained in the simulated GO structures, it is possible to unambiguously identify which groups (hydroxyls, epoxy or ethers) contribute to the carbon chemical shift in the XPS spectrum. In Figure 4 the calculated chemical shifts of the $C-1s$ orbitals are displayed, with the graphitic peak as reference³². Performing a deconvolution of the calculated $C-1s$ photoelectron peaks, four different contributions were identified: an sp^2 graphitic peak relative to $C=C$ aromatic bonds (taken as reference), a hydroxyl peak related to $C-OH$ bonds, an epoxide peak relative to carbons forming epoxides and finally an ether peak relative to carbon atoms making 1,2-ether species (see Figure 4). The shifts between the peaks of each carbon species remain almost constant when changing the degree of oxidation, only the intensity of the peaks is affected by the atomic coverage. The area under each peak is proportional to the concentration of species. Specifically, we observed that the hydroxyl peak is shifted toward higher energies by ~ 1.7 eV, the epoxide peak by ~ 1.6 eV and the ether peak by ~ 1.2 eV with respect to the graphitic peak (sp^2 contribution). These assignments are consistent with the measurements of Hossain et al.³³ relatively to the epoxide peak, and with those measured and computed, using a Δ -SCF approach, by Barinov et al.³⁴. Calculations in the latter work are performed on structures containing a few selected functional groups which does not fully represent the amorphous nature of GO.

In summary, using a combination of classical MD and all-electron DFT simulations, we have presented an extensive investigation of GO at low degrees of oxidation. We have linked the presence of different oxygen-containing species to specific electronic modifications. Moreover, we have simulated the XPS spectra of our GO samples identifying the chemical shift of each different contributions to the $C-1s$ peak by each oxygen-containing group. This represents a fundamental support for the interpretation of XPS acquisitions. Interestingly,

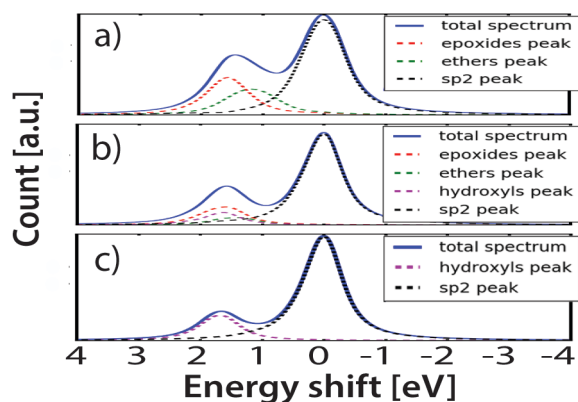


Figure 4. Simulated XPS spectra of GO with coverage $\Theta=20\%$, only epoxide and ether groups (a), 50% of epoxide/ether and 50% of hydroxyl groups (b) and only hydroxyl groups (c).

we also provide evidence for the presence of 1,2-ether groups in the basal plane of GO. To this extent we propose a revision of the Lerf-Klinowski model that also includes 1,2-ethers in the basal plane. 1,2-ethers may play an important role when devising GO chemical modifications aiming either at producing defect and oxygen free graphene or at achieving selective pore formation to obtain highly efficient single layer reverse osmosis desalination membranes³⁵. Our discoveries also highlight that being able to chemically turn $-\text{OH}$ groups into $-\text{O}-$ and vice versa in a controlled way, allows tailoring the electronic properties of GO samples and boost its usage for specific technological applications.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Detailed computational method, Bader topological analysis and supplementary data relative to corrugation and $-\text{OH}$ adsorption, including Figures S1 to S5 and Table S1. (PDF)

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Notes

The authors declare no competing financial interest.

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SYNOPSIS TOC

