

Insights into the electronic structure of oxygen-functionalized single- and bilayer graphene

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ABSTRACT

We investigate the structural and electrical properties of single-layer (SLG) and bilayer graphene (BLG) exposed to an oxygen plasma. The results of XPS spectroscopy measurements, combined with *ab initio* calculations of the density of states and electronic band structures, allow us to attribute the change in the properties of SLG and BLG to the presence of oxygen atoms on the lattice surface, in the form of epoxy groups. In detail, a bandgap appears in SLG in the case of oxygen atom densities as high as 50%, whereas BLG retains its semimetallicity. Moreover, the details of the band structure of oxygen-decorated BLG, in the immediate vicinity of the Fermi level, are practically undistinguishable from those of pristine SLG. These results are corroborated by Raman spectroscopy and electrical measurements performed on back-gated, plasma-treated graphene devices. This work represents a step forward in the controlled tailoring of the properties of graphene for electronic applications.

Keywords: graphene, oxygen plasma, X-ray photoemission spectroscopy, Raman spectroscopy, DFT calculation

INTRODUCTION

Graphene is a 2-D lattice of in-plane sp^2 -bonded carbon atoms, successfully isolated for the first time only in 2004. Due to its unique structural and electronic properties, graphene has been widely regarded as a material that could enable novel solutions in a variety of fields, such as micro- and nano-electronics, optoelectronics, sensing, etc. Being only one-atom-thin, graphene necessitates careful experimental conditions in order to be properly characterized. There are still many aspects of graphene physics still in their infancy. For example, the kinetics and dynamics of the interaction of graphene with foreign atoms is still not completely understood, especially in the cases whereby highly oxidizing species are considered.

In this work, we investigate the structural, electrical, and optical properties of BLG subjected to a mild O_2 plasma. The assumption that, upon plasma treatment, the lattice of BLG is functionalized with oxygen atoms is verified by analyzing the results of different

characterization techniques and by comparing them with the results of first principles density functional theory (DFT) calculations. Interestingly, we observed a behavior distinctively different from that of plasma-treated SLG: that is, BLG retains its semimetallicity as confirmed by electrical measurements. The DFT calculations support that no bandgap opens in oxidized BLG, even at high densities of oxygen sites, in clear contrast to oxidized SLG.

From the view point of the surface chemistry, the exact identification of the functional groups present on the graphene surface after O_2 plasma treatment is of utmost importance. To probe the chemical bond nature of the oxidized graphene surface, we first considered an equivalent system, that is highly oriented pyrolytic graphene (HOPG) samples, exposed to O_2 plasma in conditions equivalent to those used for the graphene samples discussed later in this work. After plasma treatment, the samples were annealed in an inert atmosphere (Ar) at 170 °C for 6 h. We then performed XPS measurements on the samples *ex situ*, using 1486.6 eV photons (Al K α radiation source). We analyzed both O 1s and C 1s peaks to investigate the presence of carbon-oxygen functional groups. The O 1s and C 1s XPS spectra of HOPG samples ($1 \times 1 \text{ cm}^2$) treated for short (10 s) and long times (300 s) are shown in Figure 1(a,b). Careful analysis of the O 1s and C 1s binding energies indicates that a short exposure to O_2 plasma introduces epoxy (C–O–C) and hydroxyl (C–OH) groups as the sole functional groups present on the oxidized graphene surface. In literature, these two functional groups have indeed been identified as the most favorable configurations in graphene oxide obtained by wet chemical methods.¹⁻² Epoxy and hydroxyl groups have been located mainly at the basal plane and the edges of graphene, respectively.³ Scanning probe microscopy analysis suggested that epoxy groups are arranged on the basal plane of the graphene lattice with preferentially linear alignment.⁴ Theoretical and experimental work on ozone-treated graphene also revealed the nature of epoxide groups arranged on the graphene surface.⁵

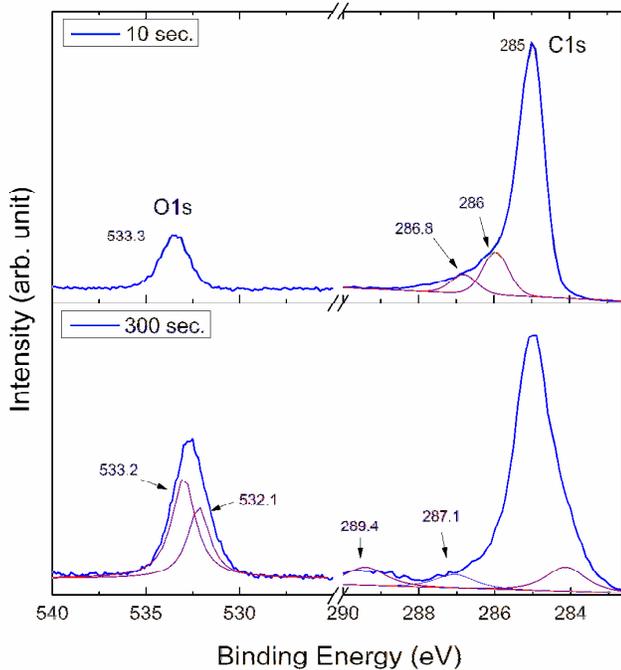


Figure 1: XPS spectra of HOPG samples exposed to O_2 plasma for 10 s and 300 s, showing the presence of O 1s and C 1s peaks.

To further evaluate the effects of the O_2 plasma treatment on the structure and optoelectronic properties of bilayer graphene, we perform first principles simulations based on DFT. DFT calculations are carried out by using the generalized gradient approximation (GGA) with a plane-wave basis and the Perdew–Burke–Ernzerhof exchange–correlation functional⁶, as used in the PWscf code available within Quantum Espresso package⁷ (450 Ry plane-wave cutoff). A $15 \times 15 \times 1$ Monkhorst–Pack grid for the sampling of the Brillouin zone is employed to compute the structural relaxations. Atomic geometries are relaxed with forces <0.02 eV/Å and stresses <0.05 GPa. We considered a 3-D unit cell in which SLG or BLG are isolated by a 15 Å vacuum, large enough to ensure negligible interaction between functionalized graphene and its periodic images.

Figure 2 plots the density of states (DOS) of SLG and BLG calculated for increasing density of epoxy groups on the surface. SLG is known to be a gapless semiconductor with vanishing DOS at the Fermi level E_F , whereas the interlayer interaction in AB stacked BLG (and also in multilayer graphene) leads to a nonvanishing DOS at E_F .⁸ Introducing epoxy groups on the SLG surface strongly affects its electronic structure. While the lowest oxygen density investigated (C_8O_1) results in no bandgap in SLG (not shown here), a further increase in the epoxy group density, *viz.* C_8O_2 , yields ~ 1.5 eV bandgap near E_F . The bandgap then increases monotonically with the epoxy group density, so that, in the case of a 50% oxygen density, *viz.* C_8O_4 , the bandgap is ~ 3.5 eV. For SLG, an increasing

oxygen density is accompanied by a progressive change of the pristine sp^2 hybridization of the carbon atoms in the SLG lattice: the sp^3 character of the C atoms in graphene increases due to the presence of the out-of-plane epoxy groups. Thus, according to DFT calculations, oxygen-decorated SLG will lose its semimetallic behavior to become semiconducting if a sufficient density of oxygen atoms, in the form of epoxy groups, are present on its surface. The introduction of oxygen-containing functional groups arranged on BLG affects the electronic properties notably differently. As depicted in Figure 2, oxidation dose not induce a bandgap near E_F pointing to a retaining of the semimetallicity. Indeed, irrespective of the oxygen density in the structure, the valley-like DOS with a nonzero minimum in the vicinity of E_F is more or less retained in the oxidized BLG

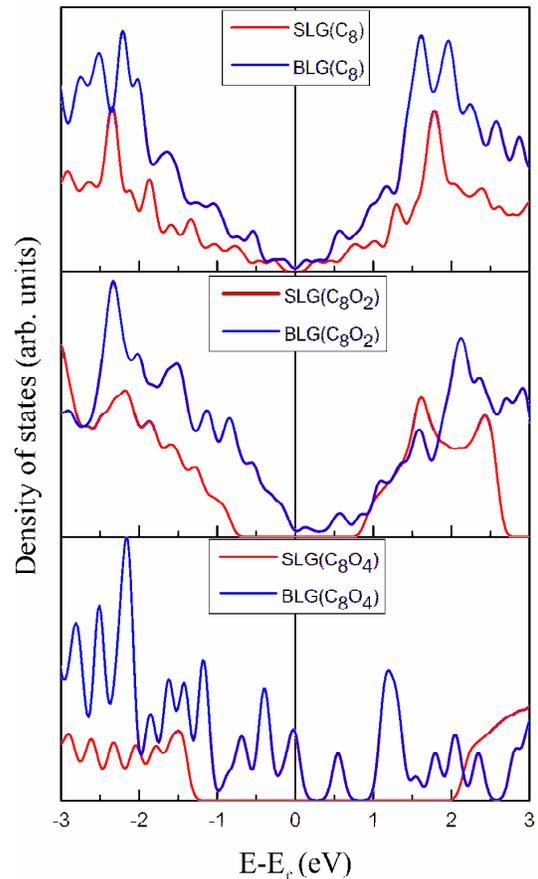


Figure 2. Total density of states (DOS) of SLG and BLG calculated for increasing epoxy group surface density. The Fermi energy E_F is set to zero.

Figure 3 compares the calculated band structure of BLG before and after decoration with epoxy groups. In the case of pristine BLG (C_8), four bands can be identified near K : two inner bands, touching at E_F , and two outer bands separated by a ~ 0.8 eV bandgap. The band energy dispersion is parabolic due to the interlayer coupling.²⁶ In the case of epoxidized BLG, we focus our attention on the features observed in the immediate vicinity of E_F ; the

following features are visible: (i) the electronic structure remains gapless; (ii) the conduction and valence inner bands become linear and touch at the Dirac point; (iii) the inner bands shift to higher energy; (iv) E_F shifts downwards with respect to the Dirac point. These features have deep consequences on both the electrical behaviour and the Raman spectra of oxidized BLG, as will be discussed further.

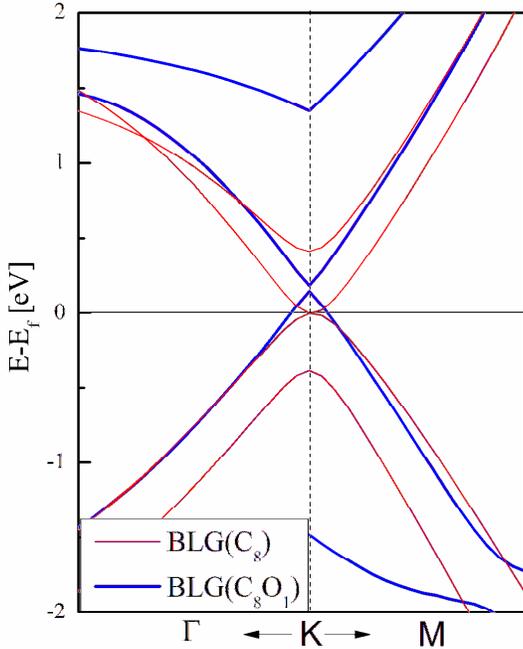


Figure 3. Electronic band structure of pristine BLG (C_8 , b), and BLG decorated with epoxide one group, C_8O_1 . The Fermi level E_F is set to zero.

We now turn to the electrical characterization of a O_2 plasma treated BLG field-effect transistor (BLG-FET), back-gated across a 300 nm SiO_2 film. Figure 4 plots the resistivity ρ_{DS} vs. back gate voltage V_{gs} before and after short exposure to an O_2 plasma. The pristine BLG-FET exhibits ambipolar characteristics and results slightly p-doped (neutrality point voltage $V_{NP} \sim -4$ V) due to the presence of contaminants and device fabrication residuals. After O_2 plasma, the ambipolarity of BLG-FET is retained and the neutrality point shifts towards more positive V_{gs} , indicating that the treated device is doped with holes, a behavior in agreement with the decrease of the Fermi level in the band structure (Figure 3) due to interaction with oxygen. The semimetallic behavior of oxidized BLG predicted from the band structure calculations in Figure 3 is experimentally confirmed when observing the low I_{on}/I_{off} ratio extracted from the transcharacteristics of the treated BLG-FET in Figure 4, not significantly different from that of a pristine SLG-FET. Note that the predicted metallic behavior in oxidized BLG, even at the highest oxygen

densities investigated, clearly contrasts with the bandgap opening in sufficiently oxidized SLG (Figure 2).

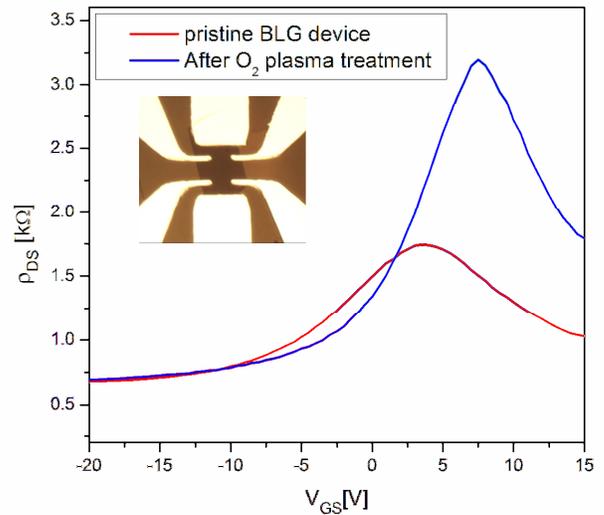


Figure 4. Transfer characteristics ρ_{DS} vs. back gate voltage V_{gs} of a BLG-FET device before and after exposure to O_2 plasma.

Figure 5 compares the full Raman spectra of pristine and O_2 plasma-treated BLG. Raman spectroscopy is a frequently applied characterization technique to probe the vibrational as well as the electronic properties of carbon materials.⁹⁻¹⁰ In the particular case of graphene, Raman spectroscopy provides more insight into the number of graphene layers, the occurrence of strain, effects of doping and defects, while it complements the information about electron-phonon scattering obtained by electrical measurements. The Raman spectrum of plasma-treated BLG (Figure 5) shows the presence of D and D' peaks, which are among the most discussed Raman features in functionalized graphene. Kudin *et al.*¹¹ calculated that out-of-plane epoxy distortions introduced in the sp^2 lattice of SLG yield D and D' peaks, as observed in the Raman spectra. We can therefore confidently attribute these two peaks, in O_2 plasma-treated BLG, to the presence of oxygen atoms covalently bonded to the BLG surface.

The most discussed feature in the Raman spectrum of graphene is the so-called 2D peak around 2700 cm^{-1} , which is attributed to a two-phonon intervalley Raman scattering process. In the case of SLG, the 2D peak consists of a single peak due to the presence of a single valence and conduction energy band for the excitation with visible light, making only a single possible two-phonon scattering process possible at K .¹² In pristine BLG, the presence of two pairs of valence and conduction energy bands, respectively, allow four two-phonon scattering events at K , giving rise to a four-component 2D peak (Figures 3 and 5)¹². As shown in Figure 3, in the case of the C_8O_1 structure, the splitting of the outer conduction and valence bands dramatically increases, leaving two inner linear intersecting bands near E_F . Consequently, laser radiation lying in the visible range is unable to excite electrons from

the outer valence band to any conduction band, and the Raman scattering process falls back in the pristine SLG case. Thus, the 2D peak of oxygen-decorated BLG is expected to resemble that of pristine SLG, and, in fact, the four-component 2D peak evolves to a single-component Lorentzian peak centered at 2694 cm^{-1} and with $\sim 50\text{ cm}^{-1}$ FWHM, in accord with our theoretical prediction. The 2D band of oxidized BLG is somewhat broader with respect to that of pristine SLG (the latter being of the order of $25\text{--}35\text{ cm}^{-1}$). Further investigation of the electron-phonon coupling in oxidized BLG is in progress to explain the distinctive behavior of the 2D peak.

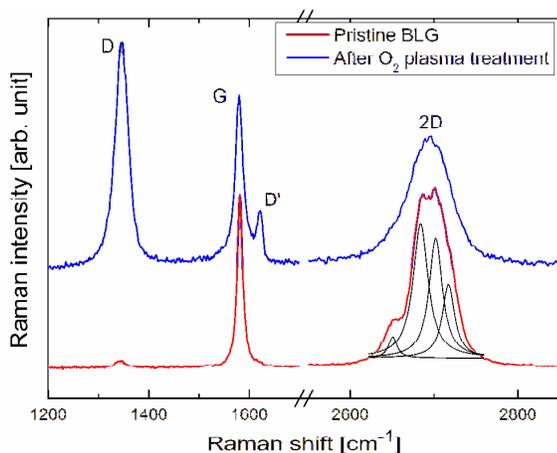


Figure 5. Raman spectra (532 nm laser excitation) collected on a pristine BLG sample (a) before and (b) after exposure to O_2 plasma. Spectra are rescaled to the intensity of the G peak

In conclusion, XPS analysis reveals the presence of C–O–C epoxy and C–OH hydroxyl groups in O_2 plasma-treated graphene. DFT calculations of DOS for epoxide-modified SLG predict a semimetallic-to-semiconducting transition in sufficiently oxidized SLG, experimentally confirmed. In contrast, oxidized BLG retains its semimetallicity, even at oxygen densities as high as 50%. Moreover, the electronic properties of O_2 plasma-treated BLG largely resemble those of pristine SLG. DFT calculations show that at low epoxy group densities, the band structures near E_F of oxidized BLG and pristine SLG are almost identical. Moreover, pristine SLG and (ep)oxidized BLG possess similar Fermi velocities. Our theoretical predictions are experimentally confirmed by electrical characterization of a O_2 plasma-treated BLG-FET, revealing a clearly semimetallic behavior, albeit to some extent hole doped. These features, together with the observed ambipolarity and nonzero minimum conductivity, are well in accord with the energy band structure calculated in the case of BLG functionalized with epoxy groups, which can therefore be assumed to be the dominant species decorating O_2 plasma treated graphene. Finally, despite the small difference in FWHM and position, the single

Lorentzian lineshape of the 2D peaks in the Raman spectra of pristine SLG and (ep)oxidized BLG also show clear resemblance. The loss of the double valence and conduction band pairs of pristine BLG near E_F upon plasma treatment, and the therewith associated four-component 2D peak, explains the evolution of such peak into a single component. We can conclude that O_2 plasma treatment represents a useful technique to tailor the properties of SLG and BLG in a controlled fashion for electronic applications.

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