
**FUNCTIONALIZATION OF GRAPHENE
WITH ATOMIC OXYGEN**

**R. Larciprete^{a*}, A. Baraldi^b, P. Lacovig^c
S. Gardonio^c and S. Lizzit^c**

^a CNR Istituto dei Sistemi Complessi, UOS Tor Vergata
Roma, Italy

^b Physics Department and CENMAT, University of Trieste, and IOM-CNR
Trieste, Italy

^cElettra - Sincrotrone Trieste S.C.p.A
Trieste, Italy

^{a*} Corresponding author: *rosanna.larciprete@isc.cnr.it*

The peculiar semimetallic character of graphene (GR) with valence and conduction bands crossing at the Dirac point is mainly incompatible with the semiconducting behavior essential for controlling conductivity in GR based devices. [1] The requirement of a gap is launching a new approach, alternative to the physical patterning required for the fabrication of C nanoribbons, that views GR as a macromolecule whose properties can be modified by attaching heteroatoms to the honeycomb scaffold. A route for tailoring the GR electronic properties is offered by the functionalization with oxidizing surface groups. [2] Fully oxidized GR behaves as an insulator while the loss of oxygen atoms results in a insulatorsemiconductor- semimetal transition. Efficient and controlled GR oxidation is achieved by exposing graphene to O atoms, which adsorb on the basal plane, at patch edges or in correspondence of unsaturated C-C bonds neighboring C vacancies or point defects. Non equivalent adsorption sites lead to different bonding configurations and thus to modified thermal stability of the chemisorbed O atoms. Determining the chemical configuration, bond arrangement and structure of functionalized GR is essential for controlling gap height, transport properties and to predict chemical and thermal properties.

In this study we employed high resolution X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption spectroscopy (NEXAS) with synchrotron radiation to follow the room temperature (RT) adsorption of O atoms on monolayer GR grown on Ir(111) in order to determine the adsorption configuration and the chemical structure of the oxidized graphene. For comparison a similar experiment was performed on high oriented pyrolytic graphite (HOPG). The experiments were performed in the ultra high vacuum chamber of the SuperESCA beamline at the Elettra synchrotron radiation facility (Trieste, Italy). Graphene was grown by ethylene (C₂H₄) pyrolysis in several cycles consisting of dosing the molecules (15 L) on the Ir(111) surface heated at 623 K followed by a flash annealing to 1423 K. Atomic oxygen was produced by a radio frequency plasma source. The oxidation of GR/Ir(111) and HOPG was performed in consecutive steps from low O coverage up to saturation. Fast XPS was combined with temperature programmed desorption to monitor the reduction of samples oxidized at different levels up to the complete deoxygenation.

We found that either on graphene and on HOPG epoxy groups, formed by O atoms adsorbed in bridge position over the C-C bonds, are the dominant surface species at low oxidation stage. It has been calculated that aligned epoxy clusters generate strain instabilities in the GR lattice which evolves by unzipping the C-C bonds at the basis of the epoxy groups and incorporating etheric O atoms in the C network. [3]. In agreement with these calculations, we found that in the case of HOPG ethers groups resulting from epoxy unzipping become progressively dominating with increasing O coverage. On the contrary, for Ir supported graphene the C-C bonds of the epoxy structures stay intact up to advanced oxidation stages and the ether surface density remains minute. Our different findings in the case of GR/Ir(111) and HOPG suggest an effective role of the metal substrate in stabilizing the epoxy structures on top of graphene. In this respect the Ir4f core level spectrum measured on the oxidized GR clearly points to a modification of the interaction between GR and the topmost Ir atoms induced by the chemisorbed oxygen atoms.

The modification of the electronic structure in the oxidized GR is evident in the valence band spectrum measured at normal emission (see Fig.1a). The π and the σ bands of the pristine GR after O adsorption appears progressively shifted and strongly damped, due to the modified bonding arrangement and charge distribution. Complementary information is provided by the NEXAFS spectra (see Fig1b). In this case the π^* feature appearing at 285.5 eV in the pristine spectrum, although strongly broadened and attenuated can be still recognized after oxidation, indicating that some π conjugation is still retained in the layer. Moreover, the strong angular dependence that emerges from the comparison of the NEXAFS spectra measured at normal and grazing incidence, expresses the presence of a sp^2 -like hexagonal structure also in the oxidized GR scaffold, likely in less oxidized domains, with the π and σ orbitals maintaining the same mutual orientation as in the pristine graphene. The formation of out of plane C-O-C σ bonds results in a strong depletion of the sp^2 character of GR, although residual regions still behaving as graphitic domains remain in the layer.

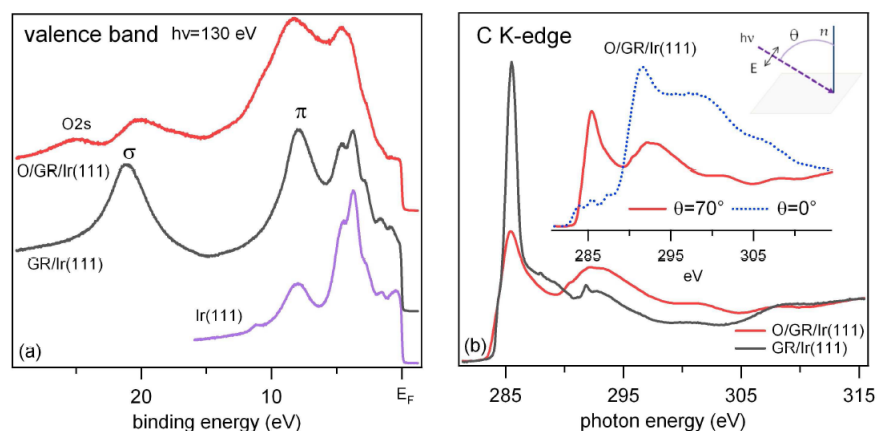


Figure 1: (a) Valence band spectra measured at normal emission on the clean Ir(111) crystal and on the pristine and fully oxidized Gr/Ir(111) surface. (b) NEXAFS spectra measured at grazing incidence ($q=70_i$) on GR/Ir(111) before and after the RT exposure to oxygen at saturation. In the inset the NEXAFS spectra measured at normal ($q=0_i$) and grazing ($q=70_i$) emission on the oxidized GR are compared

Finally we addressed the thermal stability of the oxidized GR/Ir(111) and HOPG by using fast XPS to identify the species residing at different temperatures on the sample surface and thermal programmed desorption (TPD) to reveal the molecules released in the gas phase. Results allowed us to elucidate the thermal reduction of the oxidized samples as a function of nature and surface density of the O-containing surface groups.

References

- [1] A. Geim, A. and K. Novoselov, *Nature Mater.* 6, (2007) 183
- [2] Y. Zhu et al., *Adv. Mater.* 22 (2010) 3906
- [3] J.-L Li et al., *Phys. Rev. Lett.* 96 (2006) 176101