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## SYNTHESIS AND PROPERTIES OF MONOLAYER GRAPHENE OXYFLUORIDE

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Since its discovery in 2004, graphene, a single atomic plane of carbon, has attracted a lot of scientific interest aimed to exploitation of all its potential in terms of basic research and applications. Despite all this excitement, the use of graphene for practical applications seems to be still far. For example, the absence of a band gap limits its potential for the realization of digital electronic devices and its extreme sensitivity to its environment together with a very poor selectivity makes graphene unsuitable for sensing applications. It is thus evident that a better control of graphene properties is needed for its practical exploitation. Recently, many efforts have been made to modify graphene by various atoms and molecules in order to chemically trim the electrical or mechanical properties of this material[1].

We propose a new method for the production of graphene oxyfluoride monolayers, based on a very simple electrochemical procedure that can be carried out with many chemical species thus opening the way for a wide exploration of graphene's properties by chemical functionalization. This electrochemical procedure basically follows the same recipe known by many years for the production of graphite intercalation compounds[2]. Bulk graphite, connected to a platinum wire forms an electrode that, together with a platinum counter electrode, is immersed in hydrofluoric(HF) acid 50% aqueous solution. On polarizing the graphite electrode in the positive direction, an ionic current, due to the diffusion of intercalant towards and inside the graphite planes, is established. The interaction of the intercalant species with carbon atoms composing the graphene planes is not only electrostatic, but results in various kinds of chemical bonds thus giving chemically modified graphite. After the intercalation, samples are dried and left in vacuum in order to remove HF residuals.

Electron Probe Micro-Analysis(EPMA) and X-Ray Photoelectron Spectroscopy(XPS) characterization was performed on such modified graphite in order to probe its chemical composition and the kind of chemical bonds formed between the various chemical species. In figure 1 characterization results are reported. The obtained material results being graphite mildly modified with fluorine and oxygen with concentration in the order of 3% to 6% each with good homogeneity in all the volume of the flake.

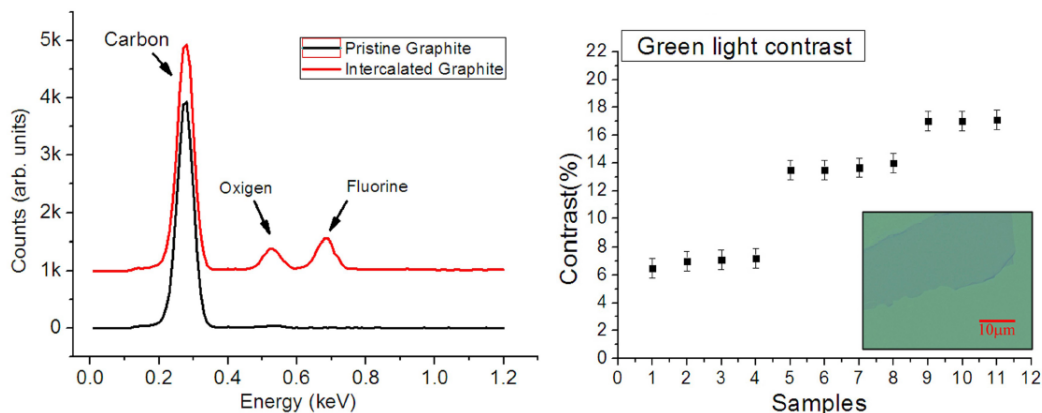


Figure 1: On the left, the comparison between EPMA spectra of pristine and modified graphite. It is possible to notice the presence of the oxygen and fluorine peaks arising upon intercalation. On the right, the contrast measurement on many exfoliated flakes. The contrast values are comparable with those of pristine graphene and varies step-like, reflecting the number of layers composing the sample.

Accurate analysis of XPS spectra showed the presence of many kinds of chemical bonds, in particular covalent and semi-ionic C-F bonds, and carbon oxidation with carbonyl and oxydril groups.

Single and few layers of oxyfluorinated graphene were extracted by micro-mechanical exfoliation and deposited on standard Si/SiO<sub>2</sub> substrates. In the right part of figure1 it is possible to see the optical contrast characterization of the deposited flakes that allows to accurately count the number of layers composing each flake, just as done with pristine graphene[3]. Raman characterization was also performed in order to study the effect of the electrochemical intercalation procedure on the Raman spectra of graphene and to check the spectra variation with the number of layers. The spectra show a pronounced D-peak, indicating structural defect in the graphene lattice, with D-peak over G-peak intensity ratios compatible with the mild modification found with EPMA.

Thanks to the large size and good homogeneity of deposited single graphene oxyfluorides flakes, it was possible to fabricate metallic contacts on them to perform a characterization of the electronic properties of such material. In figure2 it is possible to see a picture of an electronic device and its field effect characteristic showing ambipolar field effect. In comparison with pristine graphene devices, the resistivity of oxyfluorinated graphene is at least one order of magnitude higher with much lower mobilities in the order of 100 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.

In conclusion we have reported a simple electrochemical technique with which we successfully produced chemically modified oxyfluoride graphene monolayers. The suitability of such material for the realization of electronic devices, makes it very interesting for research aimed to the trimming of graphene properties for practical applications. Chemical modification could be used for inducing an electronic band-gap in graphene, and the various chemical bonds found in our oxyfluorinated graphene make it a good starting base for subsequent chemical functionalization that could lead to obtain selectivity in the electrostatic charge induction in graphene, a key parameter for sensing applications.

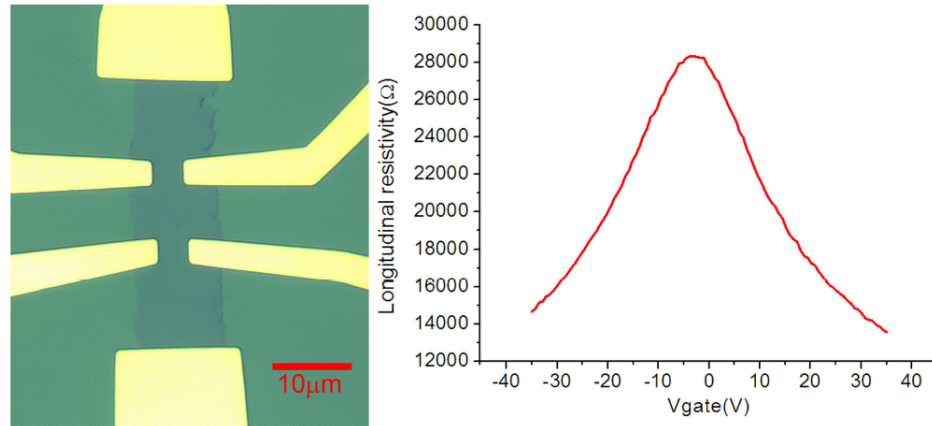


Figure 2: On the left the optical picture of an electronic device made with an oxyfluorinated graphene monolayer. Geometries were defined by electron beam lithography and then electrical contacts were fabricated by evaporating 10nm of titanium and 50nm of gold. On the right the field effect characteristic of the device at room temperature.

### References

- [1] R.R. Nair et al. ,SMALL, XX, (2010), 18
- [2] Y. Matsuo et al., Journal of Fluorine Chemistry, 87, (1998), 145150.
- [3] Bruna M. et al., J. Phys. D: Appl. Phys., 42, (2009), 175307.
- [4] Part of this work has been performed at NanoFacility Piemonte, supported by Compagnia di San Paolo.