

Reduction dependent Wetting properties of Graphene Oxide

*F. Perrozzi¹, S. Croce¹, E. Treossi^{2, 3}, V. Palermo²,
S. Santucci¹, G. Fioravanti^{1*}, L. Ottaviano^{1, 4}*

^{1*}Dipartimento di Scienze Fisiche e Chimiche, Università dell'Aquila, Via Vetoio, 67100, L'Aquila, Italy -email: giulia.fioravanti@univaq.it

²ISOF-CNR via Gobetti 101, 40129 Bologna (Italy)

³Laboratorio MIST.E-R, Via Gobetti 101, 40129, Bologna, Italy

⁴CNR-SPIN UOS L'Aquila, Via Vetoio, 67100, L'Aquila, Italy

Since its discovery, graphene family has drawn considerable attention because of its promise in the area of biomedical application, environmental health and safety[1]. The use of graphene and graphene oxide (GO) in biomaterials research is motivated by their unique surface properties which have a large effect on adsorption and dispersibility.

Many studies are focused on the biological interaction of graphene oxide because of its desirable water solubility and compatibility with biological medium, that make it an ideal candidate for potential in vivo applications[2, 3], even if there is still an open question around its toxicity[4].

The presence of oxygenated groups on the GO skeleton can be modulated by reduction (chemical, thermal, UV-irradiation...), tuning the wettability of GO thin film (see Figure 1). In this work we report contact angle measurements of standard, diol and aromatic solvents on graphene oxide thin films thermally reduced (rGO) in ultra-high vacuum up to 900 °C[5].

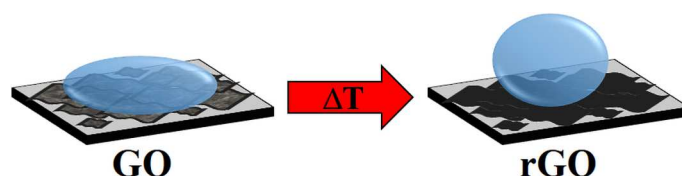


Figure 1: Wetting behavior of GO and rGO thin films.

GO thin films were prepared by spin coating at 3000 rpm the 2.5 mg/ml solution on 300 nm SiO₂/Si(100) at room temperature and in dry air. The GO thin films obtained were then reduced (rGO) at different temperatures in ultra-high vacuum (UHV, 10⁻⁹ torr).

The samples were morphologically characterized by Atomic Force Microscopy (AFM) and chemically investigated by X-ray photoelectron spectroscopy (XPS), in order to correlate the surface roughness and the chemical structure to the wetting properties of the samples. Contact angle measurements were performed in air at room temperature, dropping ~1 μL (1-2 mm in diameter) of solvent on the samples.

From a morphological point of view, our samples can be considered in good approximation planar surfaces and the wetting is homogeneous as all the samples had a RMS roughness value less than 2.9 nm and a roughness ratio of 1.006 or less. The reduction process slightly increases the smoothness of the samples, but the characterization shows that the surface roughness does not influence the wetting properties of the samples [5].

References

- [1] W. Gao et al., ACS Appl. Mater. Inter. 3 (2011) 1821.
- [2] H. Xiong, J. Photochem. Photobio. B138 (2014) 191.
- [3] H. S. Yung, ACS Nano 8 (2014) 260.
- [4] L. De Marzi et al., J. Biol. Reg. Homeos. Ag. 28 (2014) 281.
- [5] F. Perrozzi et al., Carbon 77 (2014) 473.

The different carbon functional groups contents were estimated from XPS spectra by analyzing the area of each component, such as aromatic rings and hydrogenated carbon (C=C/C-C, C-H), hydroxyl groups (C-OH), epoxy groups (C-O-C), carbonyl groups (C=O) and carboxyl groups (C=O(OH)).

The contact angle can be correlated with the chemical evolution analyzed by XPS technique. The reduction process gradually reduces the oxygen content of the samples [6], and consequently their wettability, in fact there is an increase of the value of the contact angle by increasing the reduction temperature of the samples and decreasing the oxidation degree of GO. In particular the sp^2 carbon atoms contents can be strictly correlated to the UHV annealing temperature, and thus the contact angle values can be directly related to the sp^2 content of the surface of GO.

Since the drop sizes are six orders of magnitude larger than the scale of the chemical inhomogeneity, the Cassie model is a good approximation, as confirmed by the linear trend of the cosine of the contact angle as a function of the sp^2 carbon atoms fraction[5].

For polar solvents the contact angle increases with the reduction temperature, while for nonpolar solvents (i.e. diiodomethane) it decreases (see Figure 2).

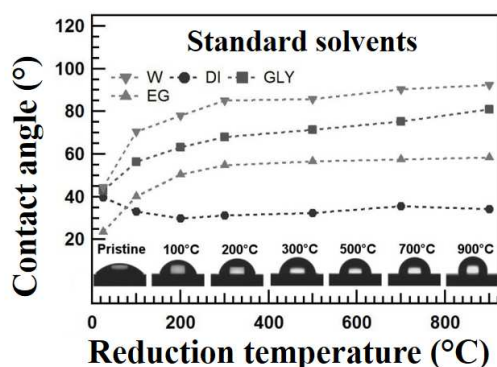


Figure 2: Contact angle measurements of standard solvents performed on GO thin films as a function of the reduction temperature (W = Water; GLY = Glycerol; EG = Ethylene Glycol; DI = Diiodomethane).

Zisman, Owens-Wendt and Neumann methods have been applied in order to calculate the surface free energy of the thin films showing that the Owens-Wendt method best fit the data trends [7]. The Owens-Wendt (OW) method provide the polar component of the SFE, a quantity that can be directly correlated with the chemical evolution (sp^2 carbon and oxygen contents) of the GO with its reduction [5].

The surface free energy varies from 51 mN/m (pristine GO) to 39 mN/m (900 °C rGO), i.e. it gradually decreases with the reduction process. Getting in more detail, the dispersive component slightly increases (from 31 to 39 mN/m) while the polar one decreases substantially until arriving at a zero value at 900 °C, as the oxygen content of the samples is reduced.

These results are very important for a microscopic understanding of the wetting properties of GO and rGO, providing a reliable SFE useful for surfaces engineering with tunable wettability properties (for example changing the chemical composition and the morphology). Furthermore this study gives a better understanding of the interfacial interaction phenomena that occur between GO and environments, which are for example fundamental for the dispersion of these nanostructures in biological media [8].

References

- [6] P. G. Ren et al., *Nanotechnology* 22 (2011) 055705.
- [7] D. K. Owens et al., *J. Appl. Polym. Sci.* 13 (1969) 1741.

[8] This research was partly supported by the FET project UPGRADE (project no. 309056) of the Graphene Flagship.