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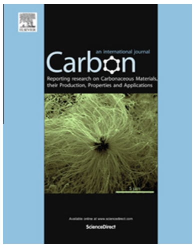

# Reduction dependent wetting properties of graphene oxide

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## ABSTRACT

This study reports contact angle measurements of standard, diol and aromatic solvents on graphene oxide thin films thermally reduced in ultra-high vacuum up to 900 °C. The films were chemically and morphologically characterized using respectively X-ray photoemission spectroscopy and atomic force microscopy. The characterization shows that the wetting occurs in the chemically heterogeneous regime, namely the surface roughness (3 nm) does not influence the wetting properties of the samples. 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. The surface free energy varies from 51 mN/m (pristine graphene oxide) to 39 mN/m (900 °C reduced graphene oxide). A correlation between the surface chemical composition, the surface free energy and its polar and dispersive components is reported, giving a rationale to the wetting properties of graphene oxide and reduced graphene oxide.

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## 1. Introduction

Graphene oxide (GO), the oxidized form of graphene, is a well-known two-dimensional material resulting from the chemical exfoliation of graphite [1]. At first proposed as a low cost precursor of graphene with scalability and low cost production potential, it has progressively become important on its own thanks to its peculiar characteristics. Indeed, though far from the outstanding physical properties of graphene, GO has its interesting properties such as tuneable optoelectronic properties thanks to reduction [2], remarkable mechanical strength [3], good water and organic solvents solubility [4] and amphiphilicity [5] and catalytic properties [6,7] GO (and reduced GO (rGO)) is therefore attractive in electro-optical [8–10], filtering [11] and biological [12] applications as well as in the construction of gas sensing devices [13,14] and composite material [15]. In some specific applications (nano-biology, coatings, printable electronics) it is fundamental the knowledge of the GO and rGO interaction with their environment (typically the solvent where the GO is diluted), i.e. the knowledge of solvent compatibility/repellency with GO surfaces. The interfacial behaviour can be analysed studying the wetting properties of such systems. In particular the surface free energy (SFE) is the fundamental physical parameter that characterizes the wetting properties of solids surfaces. The SFE is usually determined by contact angles (CA) measurements. In

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literature the wetting properties of GO and rGO have been little investigated and the results are contradictory, so far showing for example CA of water on pristine GO films ranging from 0 [16] to 60 [17] degrees. This discrepancy can be attributed to differences in the chemical compositions and in surface roughness. Furthermore the water CA decrease by increasing the oxidation degree of GO [16,17].

Indeed the determination of SFE from CA measurement is deceptively simple since what is observed is an apparent CA, not the Young CA (i.e. the thermodynamic CA on a flat and homogenous surface) from which the SFE is determined. In particular the wetting process can occur on a chemically heterogeneous surface (Cassie regime), on a rough surface (Wenzel regime), on a rough surface with trapped air bubbles (Cassie-Baxter regime), or on a surface with a mixed structure. The measured CA are therefore strongly dependent on the morphological and chemical structure of the surface. In order to correctly interpret the experiments and to determine the real SFE it is fundamental to characterize the surface and understand how far the sample is from the ideal solid surface of the Young model [16]. Furthermore there are several theoretical models that allow determining the SFE from the CA, but none of them is universally suitable for every circumstance. Moreover, in the case of graphene and related two dimensional materials, specific attention should also be paid on effects induced by the substrate (where the 2D materials are deposited), recently reported as “wetting-transparency” phenomena [17].

In this work the GO and rGO (thermally reduced in ultra-high vacuum up to 900 °C) thin films wetting properties have been studied analyzing the CA of standard, diol and aromatic solvents.

We focused on the Zisman, Owens–Wendt and Neumann models in order to study the SFE of the samples, three of the most used theories applied in the SFE determination. The thin films were carefully chemically and morphologically characterized by X-ray spectroscopy (XPS) and atomic force microscopy (AFM) respectively, in order to correlate the surface roughness and the chemical structure to the wetting properties of the samples. Furthermore it has been confirmed that the thickness of 30 nm of the GO and rGO films is enough to avoid wetting transparency effects [17]. Such a rigorous experiment and theoretical approach, to the best of our knowledge, has never been applied so far to study the wetting properties of GO.

## 2. Materials and methods

Pristine GO flakes were prepared using a modified Hummers method and dispersed in water with a concentration of 2.5 mg/mL, as described by Treossi et al. [18] The samples were prepared by spin coating at 3000 rpm the GO solution on 300 nm $SiO_2$/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 ($10^{-9}$ torr).

XPS spectra have been acquired with a PHI 1257 spectrometer equipped with a monochromatic Al Kα source ($h\nu$ = 1486.6 eV) with a pass energy of 11.75 eV, corresponding to an overall experimental resolution of 0.25 eV. The acquired XPS spectra have been fitted with Voigt line shapes and Shirley backgrounds.

**Table 1 – Solvents characteristics. All surface tension values, if not referenced, are reported in Ref. [19].**

| Name | Abbr. | Surface tension [19] (mN/m) | | |
|---|---|---|---|---|
| | | Total | Dispersive | Polar |
| Ethylene glycol | EG | 48 | 29 | 19 |
| Methylene iodide | DI | 50.8 | 50.8 | 0 |
| Glycerol | GLY | 64 | 34 | 30 |
| Water | W | 72.8 | 21.8 | 51 |
| 1,5-Pentanediol | PentDO | 43.3 | | |
| Diethylene glycol | DEG | 44.8 | | |
| 1,3-Propanediol | PDO | 46.2 | | |
| Chlorobenzene | PhCl | 33.6 [20] | 32.1 [20] | 1.5 [20] |
| Bromobenzene | PhBr | 36.5 | | |
| Benzyl alcohol | BnOH | 39 [21] | 30.3 [21] | 8.7 [21] |
| Chloronaphtalene | NCl | 39 | | |
| Bromonaphtalene | NBr | 44.4 | 44.4 | 0 |

AFM was performed in air in tapping mode using a Veeco Digital D5000 system. The microscope was equipped with silicon tips with spring constant of 3 N/m and resonance frequencies between 51 and 94 kHz.

CA measurements were performed in air at room temperature with a Kruss DSA 100 system, dropping ~1 μL (1–2 mm in diameter) of solvent on the samples with a microsyringe and acquiring the cross sectional images of the drops.

The samples were stored in high vacuum ($10^{-6}$ torr) to avoid contamination.

In Table 1 are listed the tested solvents and summarized their surface tension properties. The dispersive and polar component of the surface tension is reported whether known. The solvents are grouped in standard, diol and aromatic.

## 3. Samples characterization

### 3.1. *XPS analysis*

Chemical investigation of the GO and rGO thin films was performed using the XPS technique. In Fig. 1 (top panel) are reported the C 1s spectra of pristine GO and 900 °C rGO. All the spectra were fitted summing six components related to the following carbon functional groups: aromatic rings and hydrogenated carbon (C=C/C–C, C–H, 284.6–284.9 eV), hydroxyl groups (C–OH, 285.9 eV), epoxy groups (C–O–C, 286.9 eV), carbonyl groups (C=O, 288.2 eV), carboxyl groups (C=O(OH), 289.3 eV) and a shake-up satellite ($\pi$–$\pi^*$ transition, 290.6 eV) [22,23]. Most importantly for the sake of the present discussion, the different carbon functional groups contents can be directly estimated from XPS spectra by analyzing the area of each component (as described in detail in Ref. [22]). In particular the $sp^2$ carbon atoms contents can be strictly correlated to the UHV annealing temperature, and thus the CA values can be directly related to the $sp^2$ content of the surface of GO.

In Fig. 1 (bottom panel) are reported the oxygen and the $sp^2$ carbon atoms contents evolution. The reduction process gradually removes the oxygen functional groups decreasing the oxygen surface content from 38% in the pristine GO down

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