



Wettability and switching of electrical conductivity in UV irradiated graphene oxide films

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ABSTRACT

Graphene oxide (GO) flakes were assembled into a thin film that was subsequently exposed to UV light. It was found that pristine hydrophilic and insulating GO films present a poorer wettability together with a decrease of their surface resistivity under UV irradiation. It was observed that the pristine hydrophilic and insulating properties can be restored after few hours from irradiation. Using infrared spectroscopy and micro-Raman spectroscopy, we study the relationship between surface chemistry and structural distortion of GO films before and after UV irradiation. The obtained results open a solvent free as well as easy route for the integration of GO based materials into optoelectronic devices.

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1. Introduction

Single layer graphene sheet was first obtained by mechanical exfoliation of graphite platelets [1,2]; this method is not suitable for large scale production of graphene, for this reason the solution route consisting of exfoliation of graphite by solvents and the stabilization of exfoliated graphene in liquid suspension have been addressed as the other common method to produce graphene. The easy processing and the versatile properties of graphene oxide (GO) make the reduction methods for such material attractive for restoring the charge carrier transport typically observed for ideal graphene [3–5]. Chemical free methods for the reduction of graphene oxide have been recently obtained for example through photocatalytic action of TiO₂ [6]. Huang et al. [7] reported the flash reduction of graphene oxide films while Rao et al. [8] obtained the light radiation reduction of GO solutions. However, these latter two works deal with the use of flash lamp energies that were around 0.1–2 J/cm² and/or laser treatment of GO solutions, respectively.

The surface properties of both graphene and GO films are another important part to be investigated because in many cases, although the electrical properties are excellent for a specific application, the surface may require to be modified and engineered in the desired direction; especially for graphene when it is used in organic hybrid materials where the wettability plays an important role for its integration in

devices and/or its compatibilization with organic media. In this regard it was found that electrically insulating graphene oxide sheets are hydrophilic and switch to a hydrophobic state when they are reduced to conductive graphene sheets [9]. Graphene layers even if conductive are more difficult to wet and this fact could create problems when in optoelectronic devices a solvent cast approach is required and the graphene is one layer of the device to be integrated with other layers obtained by solvent casting [5].

Thus it is evident that the control of the wettability as well as of the conductivity of graphene oxide sheets through an external stimulus is of interest for such applications. In this work, we investigated by Raman and infrared spectroscopy the physical and chemical changes of the GO surface when it is exposed to UV radiation; we found that upon exposure to the UV light, GO films decreased their wettability along with their electrical resistivity being this effect reversible when they were left in atmospheric oxygen for several hours after UV irradiation. The method reported here suggests that the deoxygenation and subsequent oxygenation of GO films can be obtained through a clean and dry method where no chemicals are required. This investigation presents an easy route for the integration of GO based materials in optoelectronic devices.

2. Experimental

Graphene oxide was purchased from Cheaptubes (thickness 1–5 nm by AFM see Supplementary data). Water dispersion (1 mg/1 ml) was prepared and sonicated (750 W, 60% amplitude) for 1 h to yield a yellow suspension. Quartz substrates (20 mm × 20 mm; 1 mm thick) were

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cleaned by ethanol and acetone, rinsed with water, dried under nitrogen and taken inside a dry Ar glove box. Graphene oxide films were prepared by spreading the water solutions of the prepared graphene oxide sheets onto the substrates. The deposited films were then annealed at 100 °C for 1 h in vacuum (10^{-3} Torr) and air atmosphere (100 °C for 1 h, oxygen partial pressure 160 Torr, relative humidity 35%), respectively. For UV irradiation, a pencil-type Hg calibration lamp (Oriel, 30 mW/cm²) was used. The GO films were irradiated in low vacuum atmosphere (10^{-1} Torr) for 1 h and 3 h, respectively.

Contact angles were measured with an optical contact angle meter at room temperature. Water droplets were dropped carefully onto the surfaces and the contact angle was monitored. Raman spectroscopy was carried out using a Raman Bruker Senterra; the laser excitation was 532 nm and the power was kept at 5 mW. The spectra were acquired by averaging 5 acquisitions of 5 s with a 100× objective.

Fourier transform infrared spectroscopy (FTIR), in the 500–4000 cm⁻¹ range, was used to observe the surface modification of the GO functional groups. Ultraviolet–visible (UV–Vis) measurements of the deposited films were carried out with a Perkin-Elmer spectrometer Lambda 35; for all samples, a neat quartz slide was used as the reference. The morphologies of the prepared samples were investigated by atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). The electrical characterization (four probe measurements) was performed using a computer controlled Keithley 4200 Source Measure Unit. For the four probe measurements, Al electrodes (1 mm × 10 mm) having an average thickness of ~70 nm were thermally evaporated on the GO coated quartz substrates maintaining a spacing of 2 mm.

3. Results and discussion

The FESEM characterization performed on GO films before (Fig. 1a) and after UV irradiation (Fig. 1b and c) demonstrates that, upon UV exposure the graphene sheet roughness increases; in particular an area roughness change from 10 nm to 40 nm was estimated by AFM analysis for the GO and UV irradiated GO films, respectively. Corrugation effects have been previously observed for chemically converted graphene produced by reduction of graphene oxide [3,9]. Simulations suggest that different chemical addends and their arrangements may result in significant wrinkling and even bending of graphene sheets [10]. The removal of the oxygen-containing functional groups from the basal plane of graphene flake upon UV irradiation could also contribute to the change in its corrugation [11].

In order to confirm this assumption the FTIR spectra of our GO films before and after UV irradiation have been reported in Fig. 2. The GO spectrum shows bands corresponding to the C–O stretching vibrations of the COOH groups at 1740 cm⁻¹, the O–H deformations of the C–OH groups at 1350–1390 cm⁻¹, the C–O stretching vibrations at 1060–1100 cm⁻¹, and the epoxide groups at 1230 cm⁻¹ [12]. The bands of the C–O and epoxide groups were attenuated in their intensity after the UV exposure while those of the O–H and C–O functional groups were absent from the spectrum of the GO exposed to the UV light for 3 h, thus confirming the deoxygenation of our GO films. It should be mentioned that GO film exposed to UV light for 3 h and then left in air for 24 h did not show any attenuation of the bands attributed to the functional groups (Fig. 2).

The wettability behavior of GO films before and after the UV irradiation is reported in Fig. 3. The measurements were performed at room temperature and were recorded for several minutes to monitor any possible variation of the contact angle due to film inhomogeneity and/or water evaporation. The contact angle measurements of the GO film before the UV irradiation indicate a hydrophilic behavior, on the contrary an increase of the contact angle value after UV irradiation for 1 h and 3 h was observed, respectively. It should be noticed that measuring the wettability of the same sample after 24 h from its UV

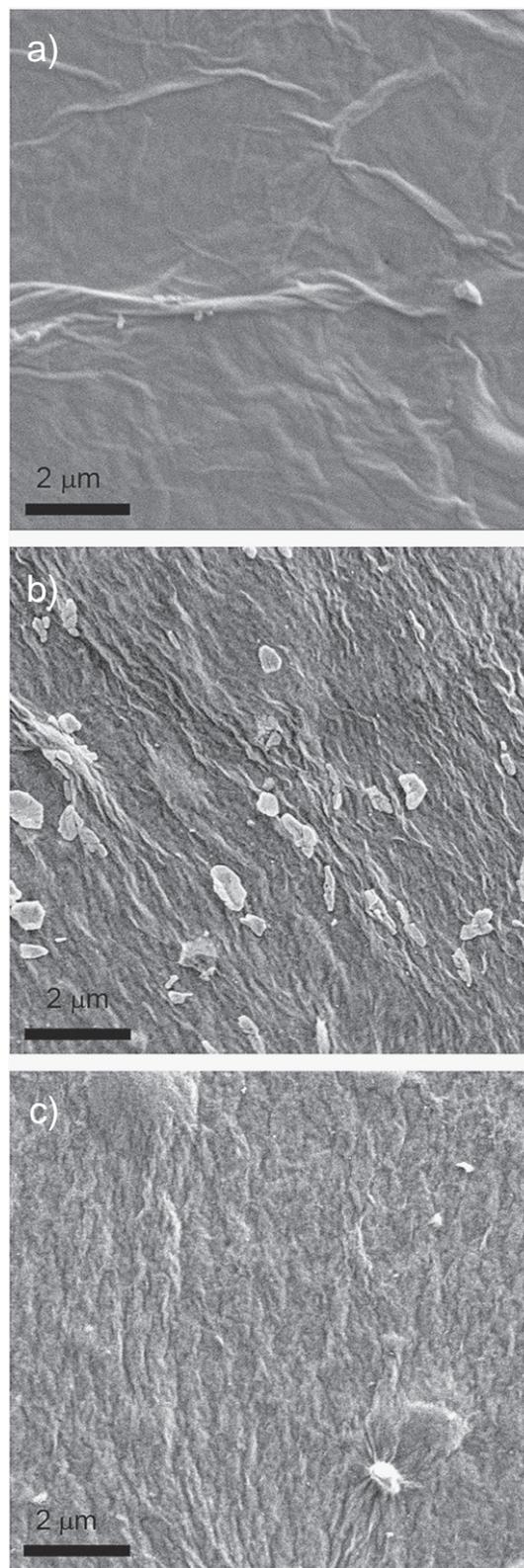


Fig. 1. FESEM images of (a) GO, (b) GO UV irradiated for 1 h and (c) GO UV irradiated for 3 h.

irradiation, the film tends to recover its initial hydrophilic behavior reaching a contact angle value of about 55°.

The hydrophilic behavior of the GO film before UV irradiation was expected accordingly to the work of Yang et al. [13] and can be explained as suggested by FTIR analysis in Fig. 2 by the presence of

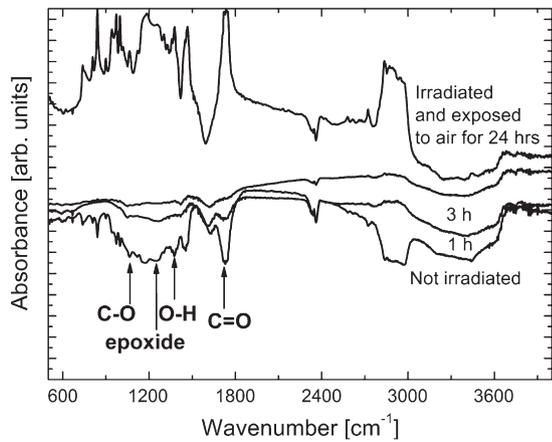


Fig. 2. FT-IR spectra showing the change of pristine GO, GO UV irradiated for 1 h, GO UV irradiated for 3 h and GO left in environmental atmosphere for several hours after UV irradiation.

carboxylic functionalities onto the GO sheets position at the film/air interface. The increase of the contact angle after the UV irradiation can be explained both in terms of deoxygenation of the GO surface (Fig. 2) and the increase of the surface roughness; the rough topography (see Fig. 1b and c) limited the contact area between the solid and liquid and air might be trapped into the cavities of the porous surface, contributing to the increased contact angle [14].

The high resistance of GO is due to the existence of oxygen-containing groups, which could introduce defects to graphene [5]. In contrast, deoxygenation could recover the GO conductivity to some extent. Recently, it has been shown that deoxygenation occurs in GO when it is heated above 100 °C, [5] resulting in a thermal reduction. Then, the sheet electrical resistance of the prepared samples was investigated. As demonstrated by the values reported in Fig. 4, it is interesting to find that after irradiation of 1 h and 3 h, respectively, the sheet resistance displays a distinct decrease. This finding suggests that the resistance of GO could be decreased via UV irradiation. During our experiments it was found that exposure to environmental atmosphere after irradiation causes an increase of the surface resistivity restoring the pristine value obtained for neat GO film. Moreover it was found that the annealing in vacuum of pristine GO did not activate the UV driven deoxygenation process leaving the GO an insulating material (i.e. 4×10^3 K Ω /sq). The decrease of the surface resistivity for air annealed and UV exposed GO samples together with

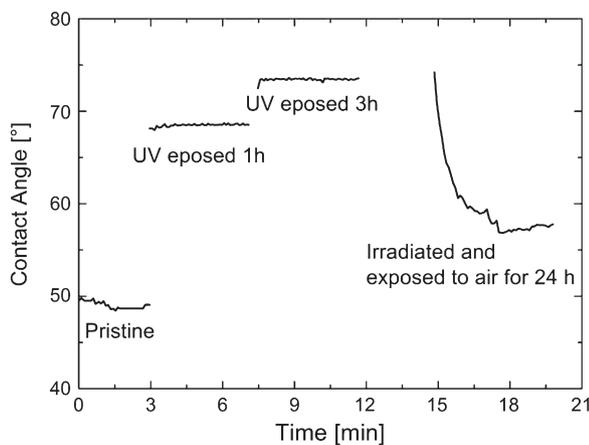


Fig. 3. Contact angle values of pristine GO, GO UV irradiated for 1 h, GO UV irradiated for 3 h and GO left in environmental atmosphere for several hours after UV irradiation.

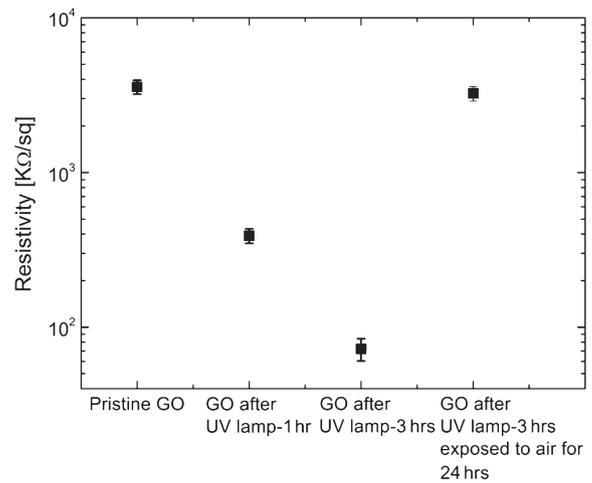


Fig. 4. Sheet resistance values of pristine GO, GO UV irradiated for 1 h, GO UV irradiated for 3 h and GO left in environmental atmosphere for several hours after UV irradiation.

the unchanged surface resistivity measured on the GO samples annealed in vacuum and then exposed to UV irradiation, suggests that the annealing in air makes the GO reactive to ground state O₂ in air and that the annealing in air induced GO surface activation mechanism around the defective sp² domains [15,16].

In order to prove these argumentations Raman analysis was used to provide further insight into the structural changes of the graphene oxide flakes, as shown in Fig. 5 [17]. The slight attenuation of the second-order zone boundary phonon (2D) peak at 2646 cm⁻¹ together with a shoulder peak at ~2920 cm⁻¹ with respect to the normalized intensity of the G band (~1590 cm⁻¹) observed for the GO film left in air for several hours after UV irradiation was due to the restoration of oxygen functional groups [18] (Fig. 5 top spectrum). Accordingly to the structural model presented by Eda et al. [5] the reduction should restore sp² carbon in GO sheet plane reducing the defects that are reactive to oxidative agents; the reduction leads to a greater connectivity among the original sp² domains reducing the intensity of the D-band (~1340 cm⁻¹) (Fig. 5 bottom spectrum) [15]. In this regard the optical images before and after Raman measurements recorded on the irradiated GO sample and left in atmospheric environment for 24 h are reported in Fig. 6. Etch pits not found on UV treated GO layer before laser treatment (Fig. 6a) were found to appear

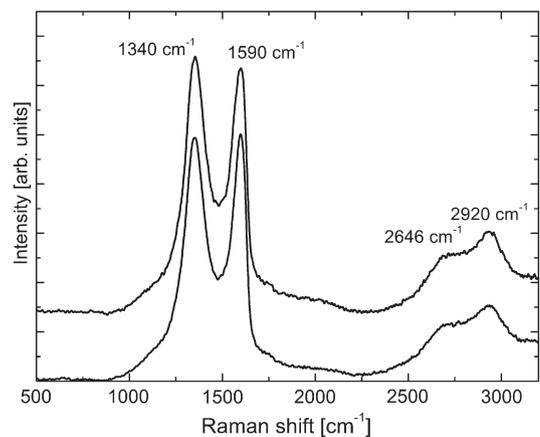


Fig. 5. Raman spectra of UV irradiated GO film (bottom spectrum) and of GO film left in air 24 h after 3 h of UV irradiation (top spectrum).

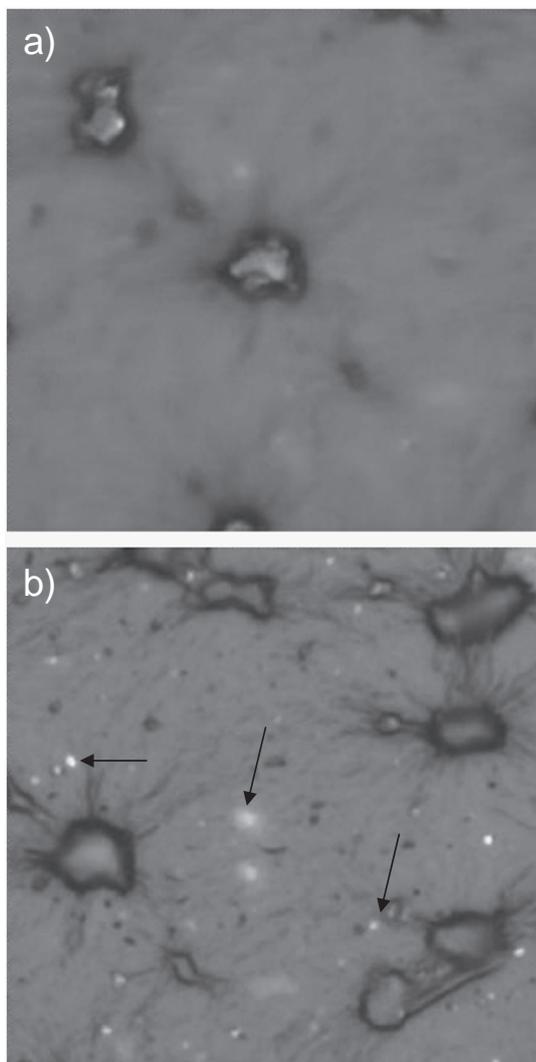


Fig. 6. Optical images of UV irradiated GO film (a) before and (b) after Raman measurement. The arrows indicate the etch pits.

after the laser exposure (Fig. 6b). This finding results from the photo-oxidative etching of defective sp^2 carbon domains activated by the atmospheric oxygen.

4. Conclusions

We characterized GO films exposed to UV light irradiation; it was found that the UV treatment is responsible of the deoxygenation of

the GO surface decreasing the electrical resistivity and changing the wettability. We showed that pristine electrical insulating and hydrophilic properties can be restored leaving our UV treated GO films in air. By comparison of micro-Raman and FTIR spectra, we found that thermal annealing in air promotes the formation of photoreactive defective sp^2 carbon domains that induce a reversible oxygen doping of the film after the UV irradiation. Considering the accessibility of graphene oxide, this study provides a possibility that this method could be used in various fields such as optoelectronic devices.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at [doi:10.1016/j.diamond.2011.04.013](https://doi.org/10.1016/j.diamond.2011.04.013).

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