

**Assessing the evolution of oxygenated functional groups on the graphene oxide surface upon
mild thermal annealing in water**

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SUPPLEMENTARY INFORMATION

DETAILS ON THE EXPERIMENTAL PROCEDURES

All the chemicals used here were of analytical reagent grade and were used as received. GO was purchased from ACS Materials, USA, and consists of single-layered graphene oxide from modified Hummers oxidation method, dispersed in water at a concentration of 5 mg mL⁻¹. This dispersion was then diluted to a 0.06 mg mL⁻¹ concentration with distilled water.^{1,2}

Thermal treatment of GO samples. 10 mL of GO samples diluted in water (0.06 mg mL⁻¹) were collected in sealed vials and placed in an oven at two temperatures, 50 and 80 °C, for different times, ranging from few hours to one week. These samples were then extracted from the oven and subject to electrochemical and spectroscopical analysis. According to the temperature used and the time of heating, the GO samples will henceforth be referred to using the following general nomenclature: GO-temperature (°C)-time (h). For example, the sample GO-80-48 was heated at 80 °C for 48h.

Preparation of graphene oxide thin films. After thermal treatment, GO thin films were obtained by drop-casting 50 µL of the GO solution onto the surface of a glassy graphite disc, for the electrochemical characterization, and onto H-terminated Si(111) surfaces for the spectroscopical analysis.^{1,2}

Electrochemical methods. The resulting graphite-supported GO deposits (0.3 cm² area) were applied as working electrodes in an electrochemical cell. An aqueous 0.1 M phosphate (K₂HPO₄/KH₂PO₄) buffered saline (PBS) solution, with pH = 7.2, was used as electrolyte, and the electrodes were an Ag/AgCl (sat., reference, E = 0.198 V vs. NHE, all potential values will henceforth be referred to this electrode) and a platinum wire (counter electrode). The samples were reduced by means of cyclic voltammetry (CV) between open circuit potential (OCP, ~0.06 V) and -1.55 V, with a potential scan rate of 20 mV s⁻¹. After electrochemical investigations, the samples were extracted from the cell and thoroughly rinsed with distilled water. All electrochemical measurements were performed using a Bio-Logic SP-150 potentiostat/galvanostat driven by the Bio-Logic EC-Lab[®] software.

X-ray photoelectron spectroscopy (XPS). The silicon-supported GO deposits underwent XPS characterization. XPS measurements were carried out using a modified Omicron NanoTechnology MXPS system equipped with a monochromatic Al K α (h ν = 1486.7 eV) X-ray source (Omicron XM-1000), operating the anode at 14 kV and 16 mA. The C 1s photoionization region was acquired using an analyzer pass energy of 20 eV and take-off angle of 21° with respect to the sample surface normal. The experimental spectra were theoretically reconstructed by fitting the secondary electrons background to a Shirley function and the elastic peaks to pseudo-Voigt functions described by a common set of parameters: position, full-width at half-maximum (FWHM), Gaussian-Lorentzian

ratio. The relative amount of the different oxygenated functional groups was determined through area ratios with an uncertainty of $\pm 10\%$.

Raman spectroscopy. Raman spectra were measured at room temperature in backscattering geometry with an inVia Renishaw micro-Raman spectrometer equipped with an air-cooled CCD detector and super-Notch filters. An Ar⁺ ion laser ($\lambda_{\text{laser}} = 514.0$ nm, estimated incident power 0.07 mW) was used, coupled to a Leica DLML microscope with a 5 \times objective. The resolution was 2 cm⁻¹ and spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. Raman spectra were acquired in several (6-10) different spots on the surface of the samples. The baseline of all spectra was subtracted and subsequently the G band was normalized to 1.

Field emission scanning electron microscopy (FESEM). Morphological investigation was performed on GO samples deposited onto H-terminated silicon surfaces using a field-emission scanning electron microscope (FE-SEM) Zeiss Auriga 405 (c/o SNN-Lab-Sapienza Nanoscience & Nanotechnology Lab).

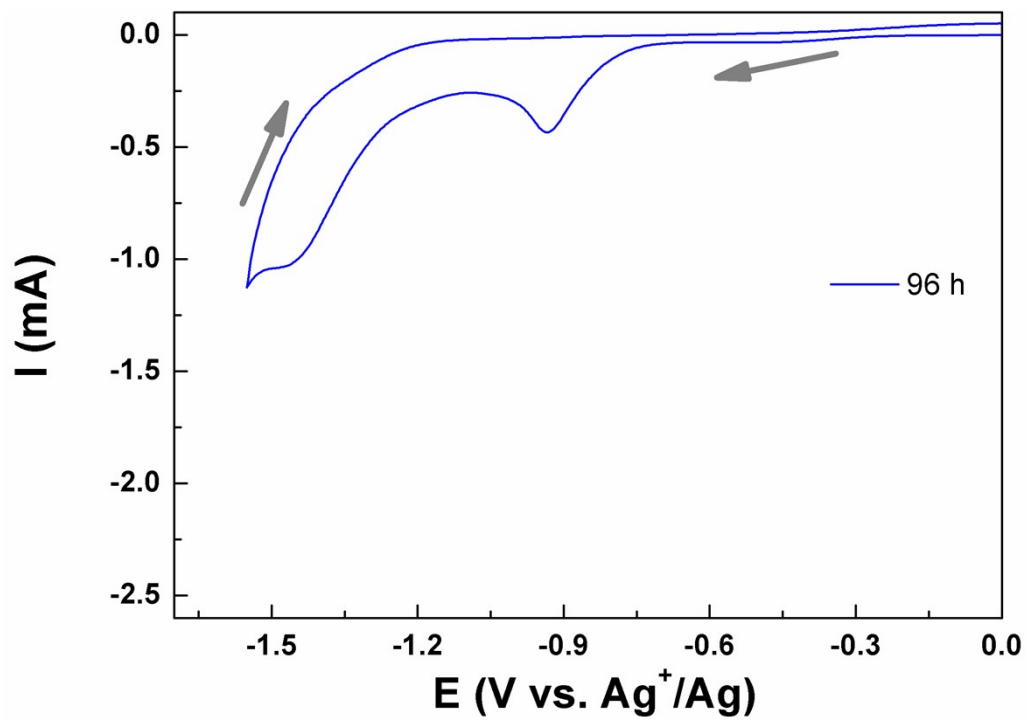


Figure S1. Cyclic voltammogram of a GO deposit from its corresponding solution thermally annealed at 50 °C for 96 h. Potential scan rate 20 mV s⁻¹.

COMPUTATIONAL METHODS

Geometry optimizations of all reactants, products, intermediates, and transition states were carried out along the entire reaction paths. Calculations were performed adopting the B3LYP hybrid GGA functional.³ The standard all-electron 6-311G** triple zeta basis set⁴ plus polarization was used for all the atoms. Unrestricted calculations were always performed owing to a RHF/UHF instability verified in some cases. Molecular geometry optimization of stationary points was carried out without symmetry constraints and using analytical gradient techniques. The transition states were searched with the synchronous, transit-guided quasi-Newton (STQN) method.⁵ Frequency analysis was performed in order to verify stationary and saddle points and to obtain thermochemical information at standard conditions (298.15 K and 1 atm). The force constants were determined analytically with the harmonic approximation. All calculations were performed using the G16 code⁶ on Linux cluster systems. Molecular graphics were produced by the CHEMCRAFT graphical package.⁷

Pristine and oxidized graphene sheets were modeled adopting a hydrogen passivated graphene cluster (Figure S2) of 48 carbon atoms (C48) as a starting point.⁸

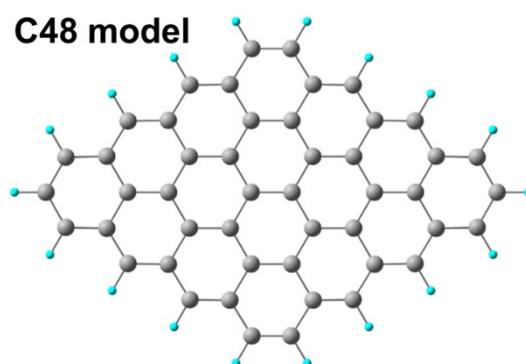


Figure S2. C48 graphene cluster used as a model in the DFT calculations.

Oxidized species were then appended on the basal plane and on the edges to model local environment on the graphene oxide sheet.

Comment on the use of XPS O 1s region to obtain quantitative/qualitative information on GO derived materials.

In general, O 1s ionization region can undoubtedly afford some kind of information in samples constituted mainly by carbon and oxygen elements. Unfortunately, this region results poorly significant in samples like those prepared in the present work. In fact, since XPS is run on GO samples drop-casted onto hydrogenated Si(111) crystal surfaces, the presence of O from SiO₂ grown onto the Si wafer is inevitably detected. Though the starting surface of the Si support is preliminarily thoroughly etched in order to remove surface silicon oxides, the contact with the aqueous droplet of the GO suspension induces a partial oxidization during the desiccation of the drop. Moreover, even if care is taken to avoid oxidation of the underlying substrate, the O 1s chemical shifts of the OFGs in GO are very small, never exceeding 1 eV, except in the case of bonds with highly electronegative or electropositive elements. This, coupled to the inherently broad FWHM of the O 1s signal, dramatically hampers a meaningful use of this region for chemical analysis in these systems. Therefore, quantification of oxygen in GO materials, whenever limited to oxygenated carbon species, is recommended to be performed from proper deconvolution of the C 1s envelope itself, using the formula reported in Table 1 of the manuscript.

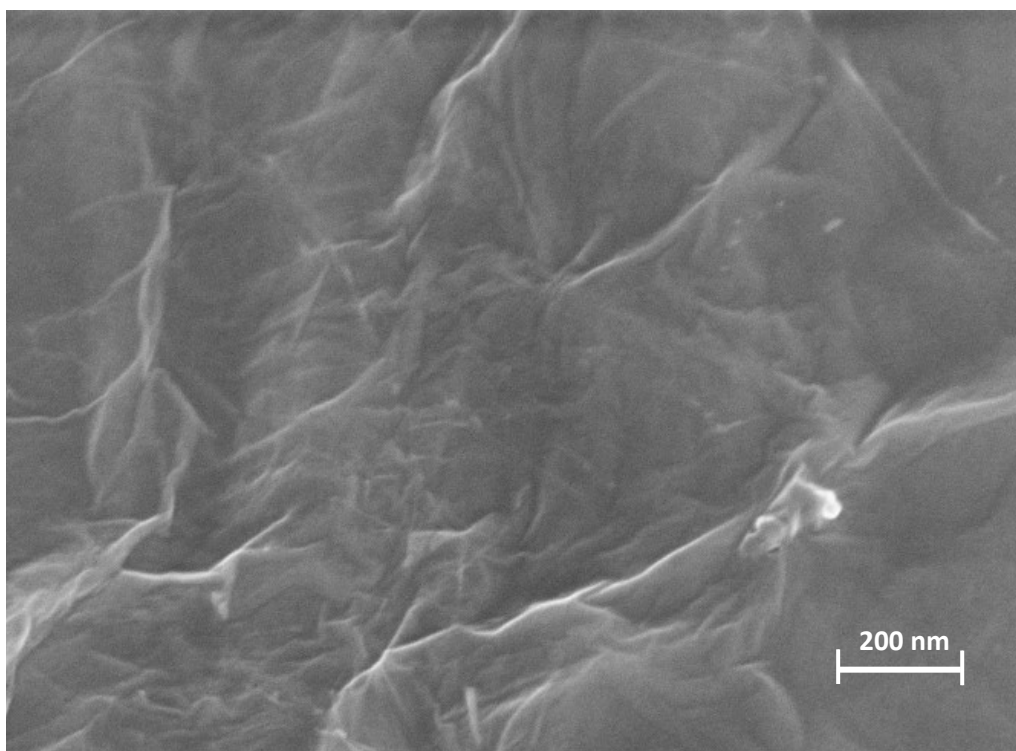


Figure S3. FE-SEM micrograph of pristine GO.

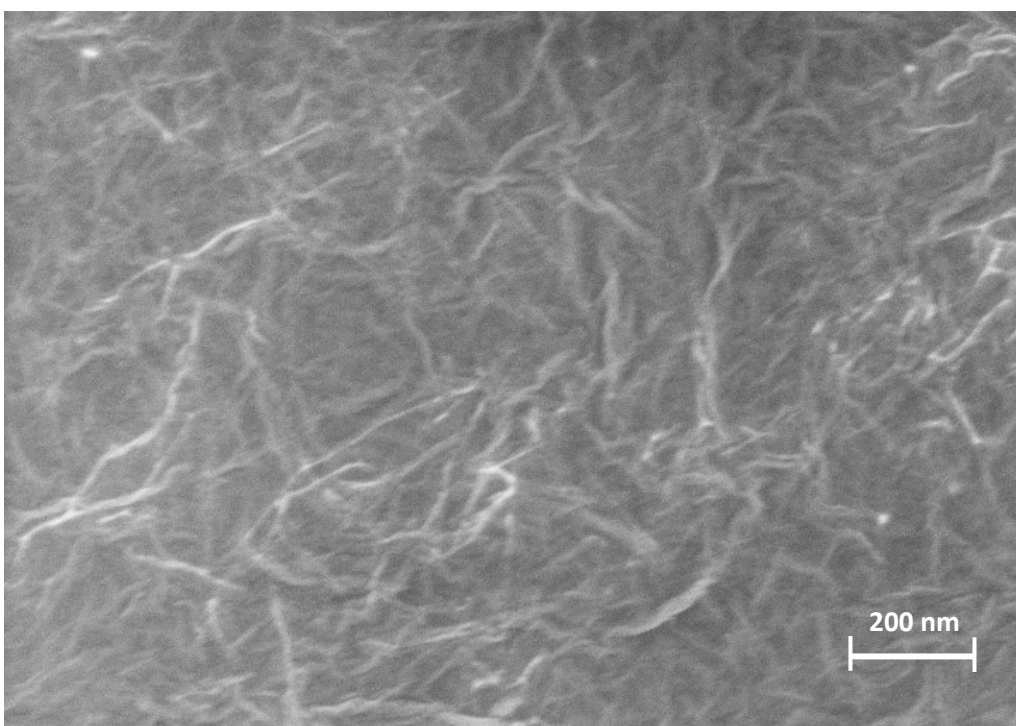


Figure S4. FE-SEM micrograph of GO-80-8 sample.

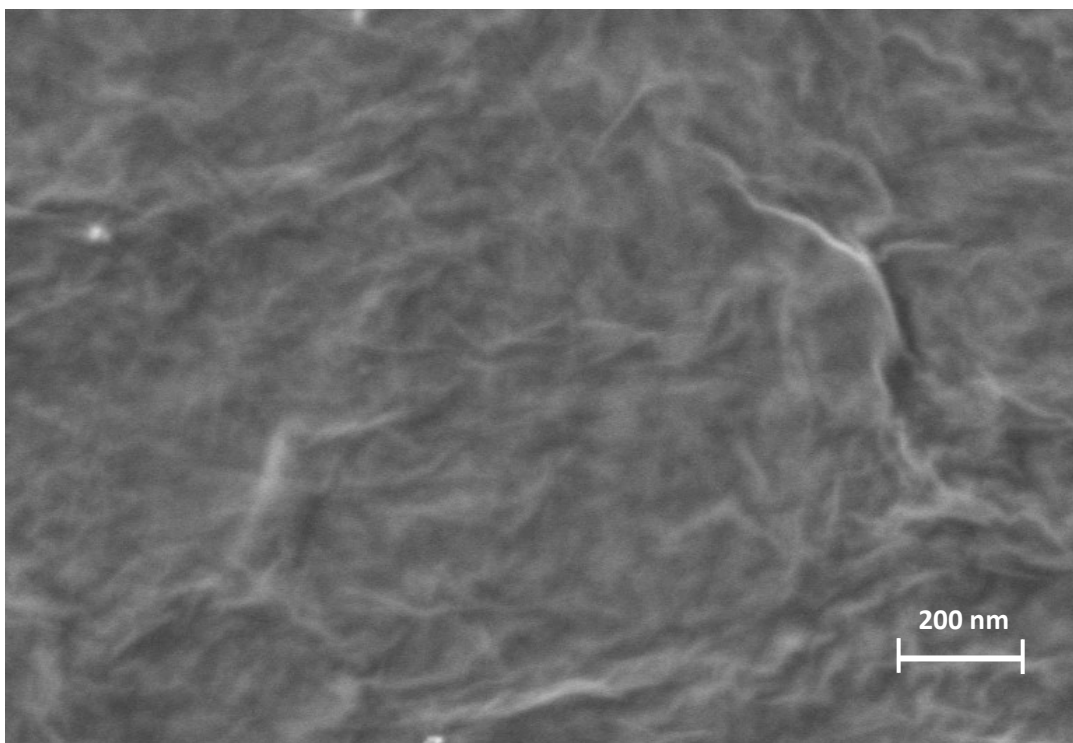


Figure S5. FE-SEM micrograph of GO-80-48 sample.

References

- 1 I. Ferrari, A. Motta, R. Zanoni, F. A. Scaramuzzo, F. Amato, E. A. Dalchiele and A. G. Marrani, *Carbon N. Y.*, 2023, **203**, 29–38.
- 2 A. G. Marrani, A. Motta, F. Amato, R. Schrebler, R. Zanoni and E. A. Dalchiele, *Nanomaterials*, 2022, **12**, 1–21.
- 3 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 4 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639–5648.
- 5 C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, , DOI:10.1002/(SICI)1096-987X(19960115)17:1.
- 6 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, 2016.
- 7 Chemcraft - graphical software for visualization of quantum chemistry computations. Version 1.8, build 654. <https://www.chemcraftprog.com>
- 8 D. Baniya, *Kathford J. Eng. Manag.*, 2018, **1**, 5–10.