
EUV-ASSISTED SPATIALLY RESOLVED GRAPHENE OXIDE REDUCTION

**S. Prezioso^{a*}, F. Perrozzi^a, M. Donarelli^a, F. Bisti^a
S. Santucci^a, M. Nardone^b, E. Treossi^c, V. Palermo^c
and L. Ottaviano^a**

^aDipartimento di Fisica, Università dell'Aquila, gc-LNGS INFN, Via Vetoio, 67100 L'Aquila, Italy

^bDipartimento di Fisica, Università dell'Aquila, Via Vetoio, 67100 L'Aquila, Italy

^cCNR-ISOF, Via Gobetti 101, 40129 Bologna, Italy

*Corresponding author: *stefano.prezioso@aquila.infn.it*

Graphene oxide (GO) is a versatile nano-layered precursor of graphene, whose selective reduction at the nanometer scale is proving to be one of the most preferable ways to get quantum confined graphene (nanoribbons and nanodots). Nanopatterns from GO reduction have been obtained using Atomic Force Microscopy by tip-induced local thermal reduction [1] or electrochemical reduction [2]. Recently, graphene microcircuits have been successfully created on GO films via direct femtosecond laser reduction [3]. Nonetheless, spatially controlled reduction of GO is still a challenging issue, especially when finalized to large area graphene-based nano-circuit integration. Here we firstly demonstrate that single-layer GO sheets deposited on Al₂O₃ thin films (72 nm thick) can be reduced by extreme ultraviolet (EUV) laser exposure ($\lambda = 46.9$ nm) with an efficiency comparable to that one of $\sim 100^\circ\text{C}$ equivalent thermal reduction in UHV. Then we demonstrate that the same effect can be spatially modulated over the GO sheets by periodical modulation of the EUV dose. Light-assisted GO reduction has been recently achieved by exposure to unfocused UV light [4,5] or by visible femtosecond-pulsed laser light exposure [3] but neither cited strategy combines the selectivity of GO patterning with large-area GO reduction, that is what we suggest in this work.

GO sheets are prepared via a modified Hummers method starting from graphite flakes of 500 μm maximum size. The resulting GO is dispersed in water and then spin-coated on 72 nm thick Al₂O₃/Si(100) preliminarily sonicated in NH₄-OH solution. The EUV light source used to reduce GO is a compact table-top laser emitting at $\lambda = 46.9$ nm. The laser pulse (1.5 ns duration, 150 μJ energy) is produced by the single pass amplification of the 3p-3s transition in Ne-like Ar in an elongated plasma column created by a fast capillary discharge. EUV dose is modulated using a simple Lloyd interferometer (Fig. 1b).

X-Ray Photoemission Spectroscopy (XPS) (monochromatic Al K α source, $h\nu = 1486.6$ eV) has been used to prove that deposited GO is reduced when illuminated by EUV radiation. The formation of graphene patches as a result of the partial GO reduction has been revealed by room temperature micro-Raman Spectroscopy (μRS) ($\lambda = 633$ nm, 1 μm spatial resolution, and ~ 2 cm⁻¹ spectral resolution). μRS has been used also to study the effects of EUV dose modulation on the GO sheets. Fig. 1a shows an image of the periodical pattern produced by the interfering EUV radiation. μRS analysis has allowed to interpret the observed pattern as an array of alternated graphene-like and GO-like stripes differing in the reduction

degree by a small percentage corresponding to few 10's °C equivalent thermal reduction. Lateral confinement expected by selective photoreduction is still an ambitious concept for such structures but what we claim here as EUV-assisted spatially resolved GO reduction opens new possibilities for graphene nano-shaping. [6]

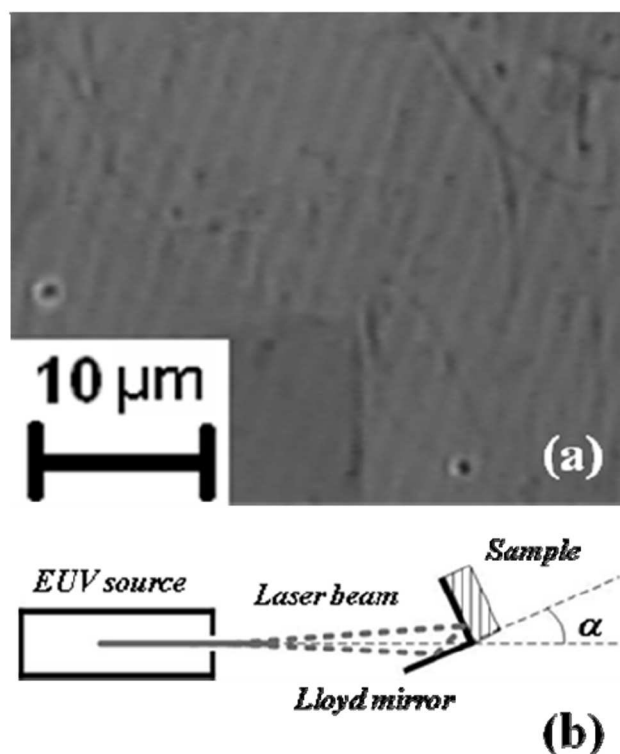


Figure 1: (a) Image of 2μm-spaced photoreduced stripes obtained on a single-layer GO sheet by periodical modulation of the radiation dose. The image have been acquired in air with an OLYMPUS optical microscope (40× objective). (b) Schematic representation of the Lloyd interferometer used to modulate the EUV dose.

References

- [1] Z. Wei, D. Wang, S. Kim S, S.-Y. Kim, Y. Hu Y, M.K. Yakes, A.R. Laracuate, Z. Dai, S.R. Marder, C. Berger, W.P. King, W.A. de Heer, P.E. Sheehan, and E. Riedo, *Science*, 328 (2010) 1373.
- [2] J. M. Mativetsky, E. Treossi, E. Orgiu, M. Melucci, G.P. Veronese, P. Samorì, and V. Palermo, *J. Am. Chem. Soc.*, 132 (2010) 14130.
- [3] Y. Zhang, L. Guo, S. Wei, Y. He, H. Xia, Q. Chen, H.-B. Sun, and F.-S. Xiao, *Nano Today*, 5 (2010) 15.
- [4] G. Williams, B. Seger, and P. V. Kamat, *ACS Nano*, 2 (2008) 1487.
- [5] S.R. Kim, K. Parvez, and M. Chhowalla, *Chem. Phys. Lett.*, 483 (2009) 124.
- [6] This research was partly supported by the Istituto Nazionale di Fisica Nucleare (INFN) project XILOPHON. S. Prezioso acknowledges individual grant from CARISPAQ (Cassa di Risparmio Provincia dell'Aquila). Authors acknowledge M. Giammatteo for technical support.