IOP Conf. Series: Journal of Physics: Conf. Series **1092** (2018) 012124 doi:10.1088/1742-6596/1092/1/012124

Reduced Graphene Oxide Nanostructures by Light: Going Beyond the Diffraction Limit

Raul D. Rodriguez*[1], Ma Bing[1], Alexey Ruban[1], Sergey Pavlov[1], Ammar Al Hamry[2], Varnika Prakash[3], Munis Khan[2], Gennadiy Murastov[1], Ashutosh Mukherjee[2], Zoheb Khan[2], Suhail Shah[2], Anna Lipovka[1], Olfa Kanoun[2], Surinder K. Mehta[3], and Evgeniya Sheremet[1]

[1]Tomsk Polytechnic University, 30 Lenin Ave, 634050 Tomsk, Russia

[2]Chemnitz University of Technology, D-09107 Chemnitz, Germany

[3]Panjab University, Chandigarh, India

*corresponding author, E-mail: raulmet@gmail.com

Abstract. Graphene oxide (GO) offers excellent possibilities that are recently demonstrated in many applications ranging from biological sensors to optoelectronic devices. The process of thermal annealing aids in removing the oxygen-containing groups in GO, making GO more graphene-like, or the so-called reduced graphene oxide (rGO). Thermal reduction can also be achieved by intense light. Here, we demonstrate a scalable, inexpensive, and environmentally friendly method to pattern graphene oxide films beyond the diffraction limit of light using a conventional laser. We show that contrary to previous reports, non-linear effects that occur under high intensity conditions of laser irradiation allow the fabrication of highly conductive carbon nanowires with dimensions much smaller than the laser spot size. The potential of this method is illustrated by the fabrication of several devices on flexible and transparent substrates, including hybrid plasmonic/rGO sensors.

1. Introduction

Similar to graphene, graphene oxide (GO) has become a hot-topic in the 2D materials community. However, in comparison to graphene, GO has low electrical conductivity due to the presence of sp^3 as well sp^2 hybridized carbon atoms. GO electrical conductivity as well as its chemical properties can be drastically enhanced by applying excess energy that removes the oxygen-containing functional groups. In this way, the sp^2 hybridization of graphene is partly restored making reduced graphene oxide (rGO) an electrical conductor. Light irradiation can be considered a form of thermal annealing [1], in particular when using a laser to generate laser-reduced graphene [2]. Besides light, there are other ways to produce rGO from GO films, that includes, an electron beam or a heated atomic force microscopy (AFM) tip. In the latter cases, it is possible to obtain submicrometer-sized patterns of rGO that can be exploited in the fabrication of micro and nanosystems including biomedical applications [3]. However, patterning by an electron beam is not scalable or inexpensive. The same goes for patterning by AFM; it is time-consuming and definitively non-scalable limiting the development of devices. In this contribution to NANOMETA 2018, we aim at developing and demonstrating an inexpensive, scalable, and faster way to produce rGO patterns from GO films deposited on any

arbitrary surface. Our method shows the additional advantage of creating conductive patterns of rGO with spatial dimensions below the laser spot size.

2. Materials and Methods

Graphene oxide commercially available from "Graphenea" was used to obtain GO films deposited by drop-coating. Different substrates were used: a rigid substrate (glass slips) and two flexible ones (PDMS and cellophane).

Different laser irradiation systems were investigated to produce the rGO patterns in lines, as shown schematically in Figure 1. A ytterbium pulsed laser engraving machine was used with 1064 nm excitation wavelength along with following parameters: laser spot 80 µm, speed rate 400 mm/s, frequency 90 kHz, pulse duration 50 ns at 5% nominal power. The second system was a portable laser engraving system with 1 W laser excitation output at 405 nm wavelength. The third method investigated involved two solid-state lasers at 785 nm and 532 nm. The Raman spectroscopy experiments were performed in a DXR™2xi Raman Imaging Microscope in the backscattering geometry with a 532 nm laser focused on the sample by a 50x LWD objective.

Spread resistance atomic force microscopy experiments were performed with a NTEGRA Prima SPM using monolithic tips made of Au. The current maps and localized IV curves were obtained in contact mode. The macro-scale conductivity was evaluated using a homemade voltage-amperometer device. After contacting the ends of rGO lines the voltage-current characteristics were recorded for samples obtained under different irradiation conditions. The (non-scaled) sketch of the laser irradiation to make conductive lines and the configuration for resistance measurements are shown in Figure 1.

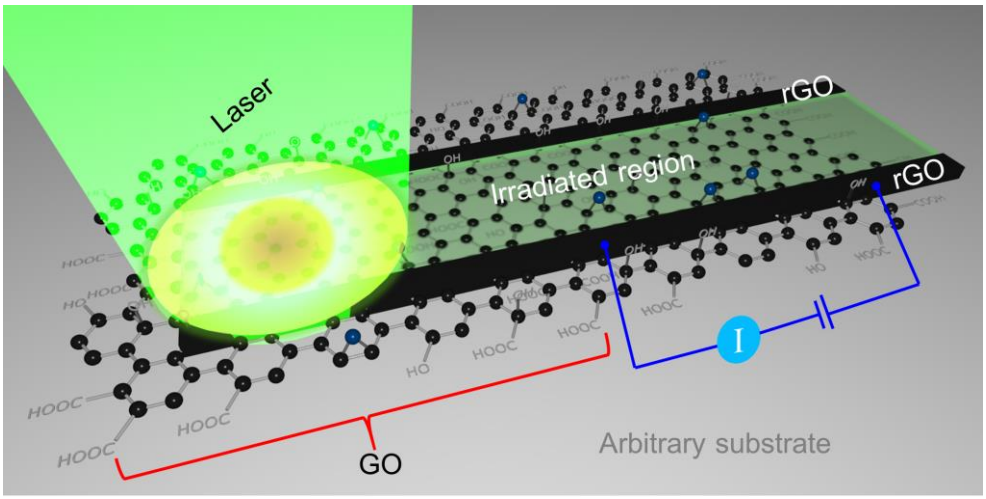

Figure 1: Schematics of the laser reduction of graphene oxide in patterned lines and the I-V characterization

3. Results and Discussion

The Figure 2a shows the conductivity map for a laser-induced pattern made on a GO film. This pattern was obtained using conventional laser annealing conditions with a 532 nm laser focused by a LWD objective (NA=0.5), and power of 8 mW. The Figure 2b is the topography map showing that there are no morphological modifications related to the laser-illuminated pattern. The Figure 2c shows the IV curves locally obtained with a metallic AFM tip used as electrode. In agreement with the conductivity map in Figure 2a, we see from the IV curve that the GO region is not conductive at all. The two other IV curves shown in Figure 2c, labelled “Conventional” and “Beyond” correspond to patterns obtained under different laser irradiation parameters, mild illumination under 532 nm, and high laser power illumination under 405 nm, respectively.

In several control samples made of linear patterns we systematically observed that: 1) there was no material remaining in the patterned lines, the laser ablated down to the plastic substrate (see Figure 3), and 2) the patterned lines showed an unexpected high electrical conductivity. To reconcile this apparent contradiction, we took a closer look at the laser-irradiated regions with Raman spectroscopy. The results obtained from dozens of spectra measured in the lines and on the pristine GO films show spectral changes that can be attributed to a modification of the carbon at the edges of the pattern (see Figure 2d and Figure 3a). Current sensing atomic force microscopy results allowed us to spatially visualize the regions responsible for the conductivity of patterns obtained under the highest laser power. These results (not shown) demonstrate that the edges were responsible for the electrical conductivity. This allowed us to conclude that by working in an extreme regime of high laser power, much higher than any reported until now in laser-reduced GO, highly confined regions of rGO could be obtained. The creation of these highly conductive edges occurred at the interface between the ablated GO regions where only the bare substrate remained, and the pristine GO at the other side of the edge. It can also be seen from the Raman microscopy image in Figure 3b that the laser spot size represented by the ablated area (blue color) is much wider in size than the thin green-bluish edges made of rGO.

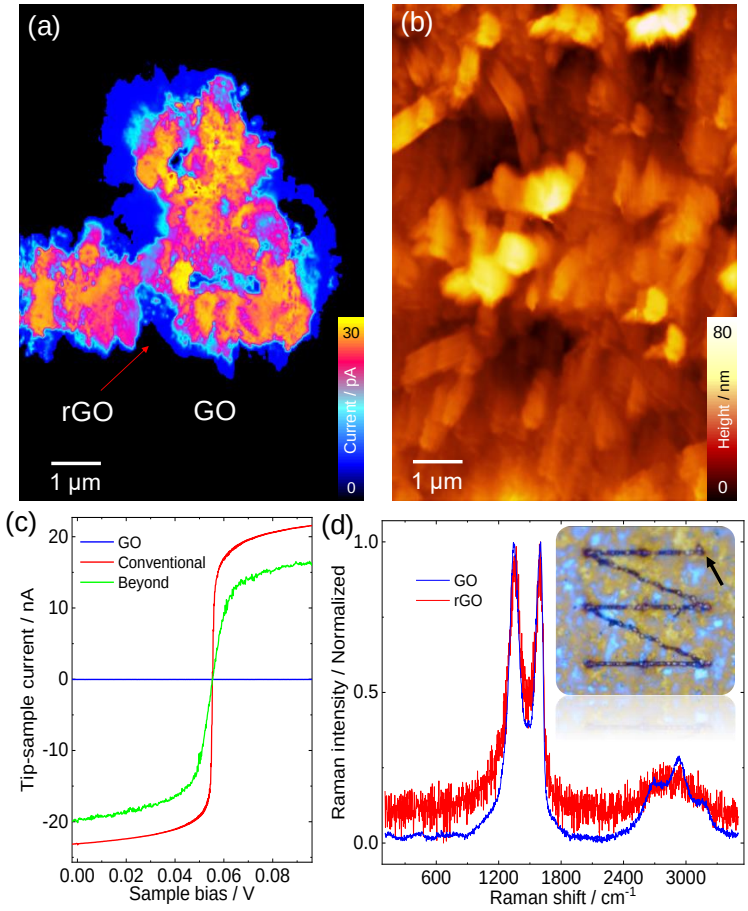

Figure 2: (a) Current sensing and (b) topography images obtained by conductive atomic force microscopy and (c) the electrical IV characterization. (d) The Raman spectra of GO and rGO; the D, G, and second order phonons show the effect of laser reduction. The inset shows a microscopy image of the laser-reduced pattern with an arrow indicated the spot imaged by AFM.

The generality and power of our method are demonstrated by the fabrication of different kinds of devices including flexible electrochemical sensors with plasmonic nanoparticles for dual-channel sensing and electronic circuits for lightings. Furthermore, this method opens the door to the creation of tunable optoelectronic devices by controlling the reversibility of the reduction process *via* an external bias. This latter is an exciting part of our ongoing research that will be briefly discussed as future perspective.

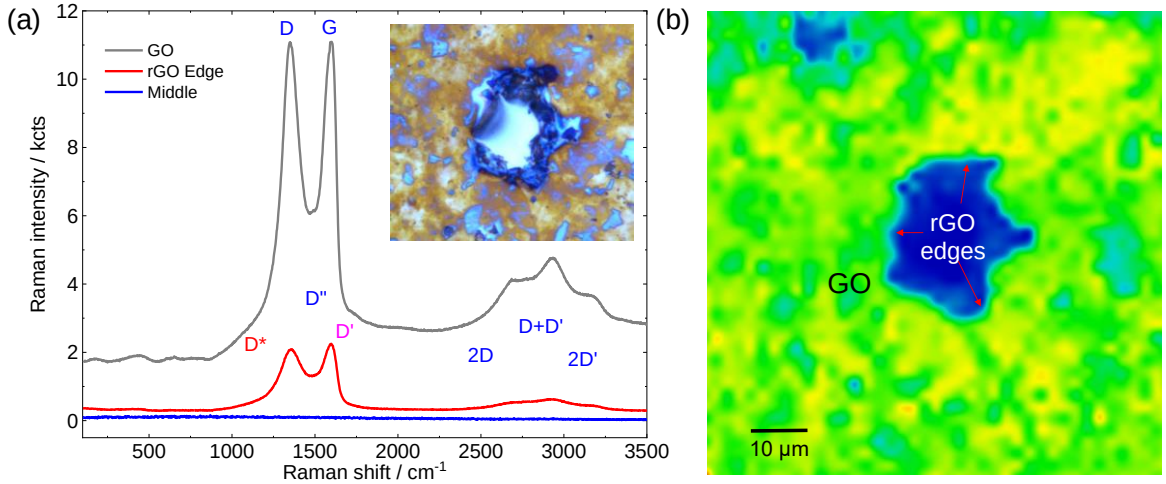

Figure 3: (a) Raman spectra from the main three regions of interest around a laser-reduced spot. The changes in intensity ratios between different peaks and the peak widths demonstrate the effects of reduction. The inset shows the optical microscopy image of the single laser irradiated spot on a GO film deposited on Au. (b) Raman intensity map for the G peak at 1590 cm^{-1}. The blue region at the middle of the spot shows no presence of GO or rGO film as also shown in the spectrum in (a).

4. Conclusion

Our research has tremendous implications in the inexpensive and large-scale fabrication of graphene-based optoelectronic devices with dimensions much smaller than the laser spot size circumventing the diffraction limit of light.

Acknowledgements

The research is carried out at Tomsk Polytechnic University within the framework of Competitiveness Enhancement Program. This work was performed in the context of the EU COST Action MP1302 Nanospectroscopy.

References

[1] A. Al-Hamry, H. Kang, E. Sowade, V. Dzhagan, R.D. Rodriguez, C. Müller, D.R.T. Zahn, R.R. Baumann, O. Kanoun, Tuning the reduction and conductivity of solution-processed graphene oxide by intense pulsed light, Carbon N. Y. 102 (2016). doi:10.1016/j.carbon.2016.02.045.

[2] Y. Zhang, L. Guo, S. Wei, Y. He, H. Xia, Q. Chen, H.B. Sun, F.S. Xiao, Direct imprinting of microcircuits on graphene oxides film by femtosecond laser reduction, Nano Today. 5 (2010) 15–20. doi:10.1016/j.nantod.2009.12.009.

[3] L. Dedelaite, R.D. Rodriguez, E. Andriukonis, M. Hietschold, D.R.T. Zahn, A. Ramanavicius, Surfaces functionalized by graphene oxide nanosheets for single cell investigations, Sensors Actuators, B Chem. (2018). doi:10.1016/j.snb.2017.08.187.