

UNDERSTANDING THE PHOTOELECTROCHEMICAL REDUCTION OF GRAPHENE OXIDE FILMS

Alan Quezada^{1,2}, Cristina Ruiz^{1*}, Luis Felipe Chazaro², Rene Rangel², Conchi Ania¹

¹*POR2E Group, CEMTHI (CNRS UPR3079) Université d'Orléans, 45071, Orléans, France*

²*Environmental Science Division. IPICYT, San Luis Potosí, México*

* cristina.ruiz-garcia@cnrs-orleans.fr

Introduction

Graphene is a carbon single layer structure that shows remarkable electronic conduction properties, and therefore offers important perspectives as sensors, energy storage and heterogeneous catalysis. Conversely, graphene oxide (GO) is the oxidized analogue, showing epoxy, hydroxyl, and carboxyl groups among others. These oxygen groups can act an important role in the functionalization of the GO by chemical modification, giving rise to a promising material in several fields of application [1]. GO can be reduced to obtain reduced graphene oxide (rGO), and depending on the experimental procedure used, the resulting rGO will show particular structural defects and electronic properties.

The present study focuses on the use of electrochemical and photochemical processes to explore the reduction of graphene oxide thin films, emphasizing on the materials characterization in terms of the elimination of O-groups and appearance of structural defects in the rGO.

Materials and Methods

Graphene oxide was prepared by the modified Hummers method [2,3] and exfoliated applying ultrasound energy in an aqueous solution. The dispersion was dropped on glass/ITO substrates, and then dried at 80 °C for 1 h after at room temperature overnight. The GO films were reduced using a solar simulator (PhrGO), electrochemical polarization in an aqueous electrolyte (ErGO), and combining both methods (EPhrGO and PhErGO). The-films were characterized by UV-vis, Raman and X-ray photoelectron spectroscopies (XPS), temperature-programmed desorption coupled to a mass spectrometer (TPD/MS), nuclear reaction analysis, among most representative techniques.

Results and Discussion

The preparation of the films by drop-casting of an aqueous suspension of GO onto a conductive support (e.g. ITO glass slide) allowed to obtain thin films of about 200-500 nm thickness on average. This allowed the use of the films directly to explore the impact of the photochemical and electrochemical approaches in the composition and structure of the rGO. The modifications of the optical properties of the graphene oxide before and after the different reduction treatments were studied by UV-Vis spectroscopy, which showed important differences between the rGO and GO films. While the pristine GO exhibited a pronounced band (*ca.* 340 nm) related with the C-O transitions, the intensity of the band decreased for PhrGO and ErGO films, and almost disappeared for Ph-ErGO. This confirmed the considerable removal of C-O moieties upon the different electrochemical and photochemical treatments. This observation was corroborated by XPS and the evolution of the C 1s core level spectra of the reduced films. Indeed, the intensity of

the band corresponding to the energy bindings for the C-O bonds (289-286 eV) is especially relevant for the pristine GO film. In contrast, in the case of EPhrGO and PhrGO films the relative abundance of this band was much lower, with still some contributions of the bands attributed to the presence of hydroxyls, carbonyls and carboxylic groups. Thus, indicating that the reduction of the surface oxygen functionalities is not complete, as reminiscent groups are still present in these films.

More interestingly, the contribution of the oxygen groups in the film obtained by electrochemical reduction was quite similar to the starting GO film. Indeed, the deconvolution of the C 1s and O 1s spectra indicated that the photochemical reduction was more effective than the electrochemical treatment to remove the oxygen content of the films, being also selective towards the removal of most labile groups. On the other hand, the study of the Raman spectroscopy showed that the band D' is less intense for the electroreduced films, and consequently the disorder in the graphitic lattice has less impact on the graphenic structure.

Conclusions

GO thin films of about 200-500 nm thickness were prepared by drop-casting of aqueous suspensions of GO onto a conductive support. Various electrochemical and photochemical approaches were used to prepare rGO films, that were further characterized using several techniques to evaluate the impact of the reduction treatment in both the composition and the structure of the resulting rGO films. Data showed that epoxide groups can be selectively removed upon mild reduction conditions. The photochemical reduction using simulated solar light was quite efficient, giving raise to higher C-C sp² contents but a larger number of structural defects in the carbon matrix.

Acknowledgment

This study was funded by the European Research Area (ERC) through Project ERC-Consolidator Grant (PHOROSOL, grant 648161).

References

1. Geim, A.K., Novoselov, K.S. (2007). The rise of graphene. *Nature Materials* 6, 183–191.
2. Hummers W. S., Offeman R. E. (1958). Preparation of graphitic oxide. *J. Am. Chem. Soc.* 80, 1339–1339.
3. Botas C., Álvarez P., Blanco P., Granda M., Blanco C., Santamaría R., Romasanta L.J., Verdejo R., López-Manchado M.A., Menéndez R. (2013). Graphene materials with different structures prepared from the same graphite by the Hummers and Brodie methods. *Carbon* 52, 156–164.