

Graphene oxides from graphites of different crystallinity

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In the last few years much attention has been devoted to the synthesis of graphenes by different methods (1, 2), and especially to the study on the electrical behavior of graphene with a view to its potential applications. Graphenes, graphene oxides (GO) and chemically modified graphenes (CMG) or partially reduced graphene oxides (GO-r) are promising materials that offer a wide range of users.

The preparation of graphene by chemical methods offers the possibility of producing high volumes of this product and also of obtaining graphene of different characteristics, depending on the parent graphite and the method used for the oxidation, and the final reduction of graphene oxide to graphene. Moreover, the defects originated during oxidation and/or chemical reduction processes yield a material with a structure in need of further chemical modification.

Despite the huge number of papers published about graphene, there is little information concerning the effect of the graphite precursor used (3). It is generally accepted that there is a need for more experimental work on the properties of isolated carbon crystallites, because polymeric carbons contain a blend of graphite crystalline structures of various sizes, amorphous phases, and high defect populations and, hence, the properties measured represent the global properties of all the constituents taken together.

The objective of this paper is to study the effect of the crystallinity of parent graphite on the reactivity of the material under the oxidation conditions required for graphene oxides preparation by using graphites of a rather different homogeneous crystallinity (G1- flow domains-, GC – mosaic - and G2 – fine mosaics-) with an increased amount of defects (Figure 1). Microscopy in its different forms (OM, SEM, TEM, AFM) and spectroscopy (Raman, XPS) are the main tools used for the characterization of the graphene oxides and partially reduced graphene oxides.

Graphene oxides were prepared from synthetic graphites by Hummer's method (4), with some modifications. Ultrasonication in water was used to separate the individual graphene oxide sheets. The three oxides are highly hydrophilic, showing good dispersion in water where they remain for along the time of the experiment (Figure 2). According to the XPS results, oxygen is mainly in the form of epoxy groups in the three oxides, with a slightly lower amount in the case of GO-C, which has a larger quantity of hydroxyls and carboxylic functionalities. This is the first indication of the different chemical reactivity of graphites in oxidation conditions. The reduction of the three oxides was performed with hydrazine, as the main feature of the end being that the partially reduced graphene oxide obtained from GO-1 was highly hydrophobic with a greater tendency to associate while those from GO-2 and GO-C showed a good dispersion in water. Under the same conditions the reduction was more effective in GO-1, yielding a partially reduced oxide (GO-1-r) with a C/O ratio of 11 while in the other two the ratio was about 5. Hydroxyl groups were dominant, ranging from 22 % in GO-1-r to 28-29 % in GO-2-r and GO-C-r. Raman spectroscopy results point to the same findings, GO-1 showing a lower ID/IG band with a value of 0.89, whereas GO-2 and GO-C show values of ID/IG, 0.91 and 0.92, respectively. This indicates a larger presence of defects in GO-2, which was obtained from the graphite of lower crystallinity.

SEM was not the best technique for observing the samples but it was of extraordinary help in determining the effectiveness of the cleaning step for removing products from the oxidation reaction and unreacted samples, as these were used in excess. For the same reason and maybe because of the

more extended functionalization, GO-2 was the most difficult to clean, requiring additional washing and ultracentrifugation steps.

In general terms, images obtained by TEM show a wrinkled paper-like structure (Figure 2b) of monolayers and no appreciable differences between the different oxides and partially reduced ones were observed.

AFM characterization confirms the greatest presence of monolayers or single sheets in the three oxides. Sheets size distribution was determined, as a certain tendency to lateral association was observed in GO-2r. These results demonstrate that control of the characteristics of the parent graphite made it possible to control the characteristics of the GOs and therefore, of the GO-rs.

References

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Acknowledgements: The authors thank Ministry of Science and Innovation (CONSOLIDER CSD2009-00500, and Ramon y Cajal program) and FICYT (postgraduate grant) for financial support.

Figures

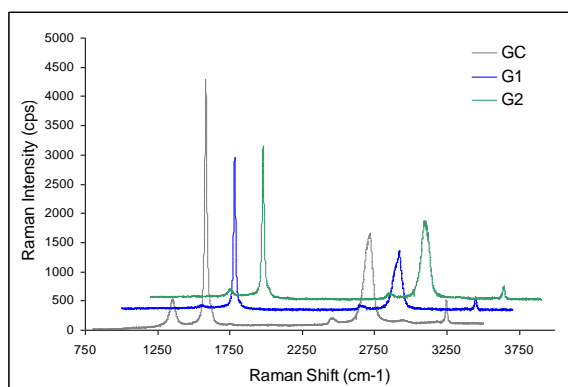


Figure 1: Raman spectra of graphite G1, GC and G2.

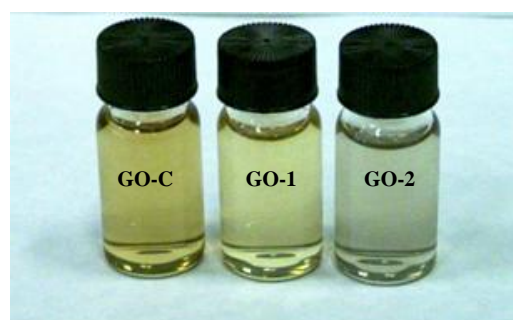


Figure 2: Image of stable dispersions of graphene oxides.

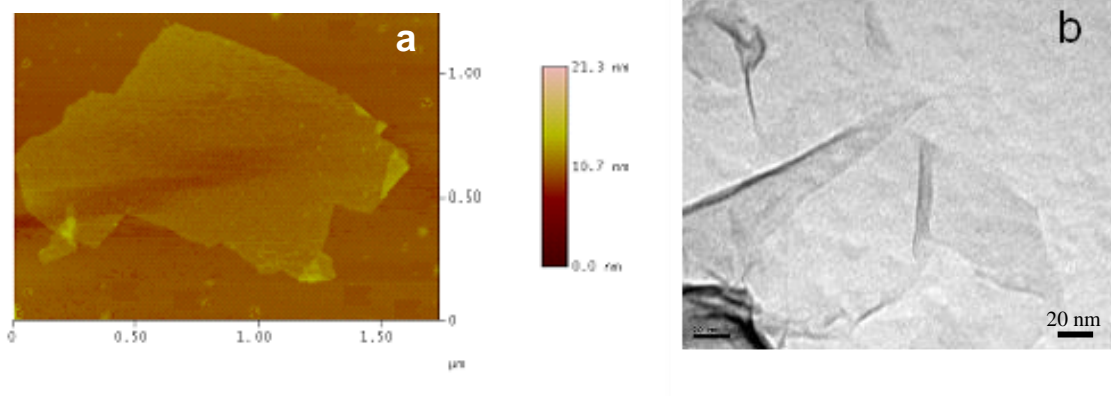


Figure 3. AFM of a single sheet of graphene oxide GO-C (a) and TEM of the same partially reduced oxide (b).