Different chemical approaches to produce graphene derivatives

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The exfoliation of graphite to obtain graphene oxide (a procedure based on the Hummers, Brodie or Staudenmaier methods [1-3]) is nowadays the most widely applied top-down strategy for the preparation of graphenes of different quality, mainly due to its scalability, low cost and the availability of a considerable amount of bibliographic information on the process. By using specifically prepared graphites with controlled crystal properties from the same precursor, we have demonstrated experimentally that the crystalline structure of the starting graphite has a marked influence on the structure of graphene oxides and also on the average area of the sheets. Once the graphene oxide is obtained, a reduction process is required in order to produce thinner flakes through the elimination of the oxygen functional groups (heat treatment assisted with a mixture of Ar and hydrogen, hydrazine, etc) [4-5]. However, the reduction mechanisms and their effects on the properties of the final graphene materials have still not been clarified.

We present some of the results (in collaboration with IREC, UAL and ICMB) of our study on the effect of graphene oxide structure (degree of structural perfection, type of oxygen functional groups and location) on its behavior when is subjected to these types of reduction process: i) chemical reduction with hydrazine, ii) thermal reduction and iii) reduction with hydrogen.

In the case of reduction with hydrazine and hydrogen, we have experimentally proved the theoretical model of Gao et al. [6] who attributed a more effective deoxygenation to the oxygen functional groups located at the interior of the aromatic domains than to those located at the edges. The reduced graphene oxides exhibited a very different atomic structure and stacking tendency. The location of the remaining hydroxyl groups at the edges in one of the materials propitiated lateral interactions which brought about a substantial increase in the size of the sheets (Figure 1). Furthermore, in collaboration with ITQ, we have demonstrated that one way to restore the graphene structure after the chemical reduction of graphene oxide would be to reconstruct of the C sp2-hybridized bonds by using carbon monoxide.

The exfoliation and thermal reduction of graphene oxides offers a simple and clean way to obtain graphenes. We have performed studies on the effect of temperature (from 120 º C to 2,400 º C), on the exfoliation/reduction behavior of the graphite oxide and have been identified the critical factors related to the efficiency and quality of the products (Figure 2). The results obtained show that the exfoliation temperature and the effectiveness of the thermal reduction are largely dependent on the chemical structure of the graphene oxide (type of functional groups and location) which in turn depends on the characteristics of the parent graphite. Moreover, it was found that the use of temperatures above 1000 ºC not only improve the structural order of the graphene sheets but also facilitate stacking, though they fail to promote the recovery of the interactions characteristics of the parent graphites (Figure 3).

Hydrogenation of the graphene oxides also proved to be an effective way to eliminate the oxygen functional groups. However, unlike thermal reduction, this methodology produces an increase of the C-Sp^3 carbon structure. We also determined the critical ranges of temperatures that produce the main

structural changes in the graphene oxide, being 150 and 200 ºC the initial temperature of elimination of the main functional groups in the graphene and 500-600 ºC when the re-ordering of the graphene layers occurs.

References

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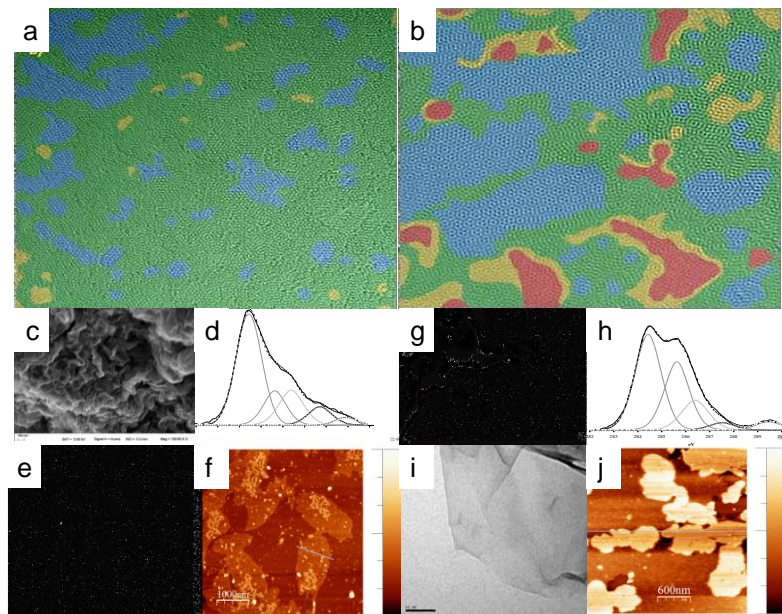
Figure1

Figure 1: Example of the different composition of the graphene layer, measured by HRTEM (a and b), that conditioned the morphology of the partially reduced graphene upon reduction with hydrazine (SEM , TEM AFM images and C1s XPS results (c,e,f,d respectively) of the partially reduced graphene corresponding to the graphene oxide (a) and g,h,I,j corresponding to the precursor (b)).
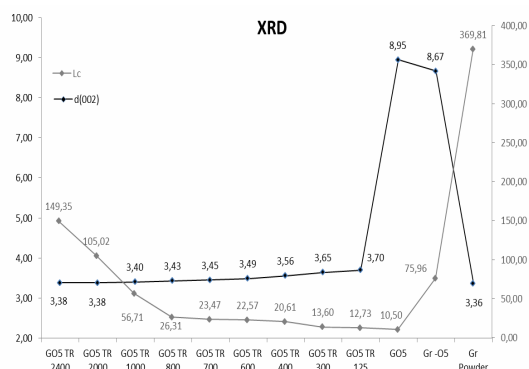
Figure2

Figure 2: XRD results showing the variation of Lc and d(002) values with temperature reduction of GO
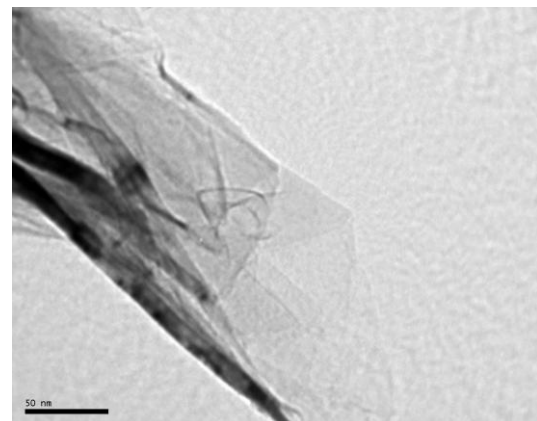
Figure 3

Figure 3: TEM image of graphite oxide thermally reduced at 2400ºC.