Preparation of graphenic materials of different structure

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Abstract

A summary of the activities of the Composites Group in the field of graphenic materials is presented. These activities include: i) the use of the chemical route through the oxidation of graphites of very different crystalline structure to obtain graphene oxides; ii) the reduction of the graphene oxides by thermal treatment, with hydrazine or with hydrogen and iii) the mechanical exfoliation of highly crystalline graphites. A detailed study on the structural changes of the different materials in the whole chain graphite-graphite oxide-graphene oxide-reduced graphene oxide by spectroscopic (Raman, FTIR, XPS, X-ray diffraction) and microscopy techniques (SEM, TEM, HR-TEM, AFM) provide novel information about the effect of the parent graphite and processing conditions on the characteristics of graphenic materials.

Two different approaches can be used to prepare graphene: the so-called top-down and bottom-up methods[1]. The top-down strategy involves carbon sources of a large size that are cut into graphene nanoplatelets. Examples of these are to be found in the mechanical cleavage of graphite[2,3], the exfoliation of graphite (via graphite oxides and intercalation compounds, so-called chemical approach)[4] or the longitudinal unzipping of carbon nanotubes[5]. This work describes the approaches used by our group to produce graphenic materials with different characteristics. Graphenes obtained by successive peeling of highly oriented graphites with different angular spread of the crystallite c-axes have shown an excellent behaviour as components in microwave frequency multiplication systems[6]. This work is part of collaboration with the Department of Electrical Engineering at the University of Oviedo. The advantage of this method is that it yields graphene layers of a high quality. The size and shape of the graphene flakes are heavily dependent on the graphite's crystalline structure. Its main limitation is related to its scalability, and to date it has only been used in fundamental laboratory studies**.**

The exfoliation of graphite to produce graphene oxide (based on the Hummers[7], Brodie[8] or Staudenmaier[9] methods) is nowadays the most widely applied top-down strategy for the preparation of graphenic materials of different structure, mainly due to its scalability and low cost. By using specifically prepared graphites from the same precursor with controlled crystal properties, it was demonstrated experimentally that the crystalline structure of the initial graphite has a marked influence on the atomic structure of graphene oxides and also on the average area of the sheets. [10]

The reduction of graphene oxides is required in order to produce thinner flakes through the elimination of the oxygen functional groups (heat treatment, hydrogen, hydrazine, etc) [11,12]. In collaboration with Catalonia Institute for Energy Research (IREC) and the Institute of Materials Science of CSIC in Barcelona (ICMB), we have studied the effect of graphene oxide atomic structure (degree of structural perfection, type of oxygen functional groups and location) on its behaviour upon reduction with hydrazine, and on the characteristics of resultant reduced graphene oxides. It was experimentally proved the theoretical model of Gao et al[13] who claim that deoxygenation is more effective when the oxygen functional groups are located in the interior of the aromatic domains than when located at the edges. The reduced graphene oxides exhibited a very different atomic structure and stacking tendency

(Figure 1). 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. Furthermore, in collaboration with ITQ-CSIC, the graphene structure was restored after the chemical reduction, through the reconstruction of the C sp^2-hybridized bonds with carbon monoxide.[14]

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 behaviour of graphite oxides (Figure 2), determining the critical temperatures that affect the efficiency of the process and quality of the products. 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, employing temperatures above 1000 ºC improves the structural order of the graphene sheets although facilitates their stacking

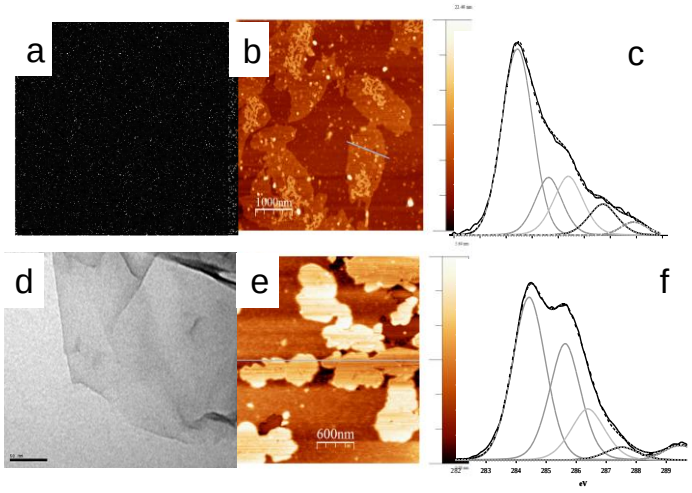

Figure 1: TEM (a) (d), AFM (b) (e) images and XPS 1CS results (c) (f) showing twopartially reduced graphene oxides obtained from graphites of different crystallinity.

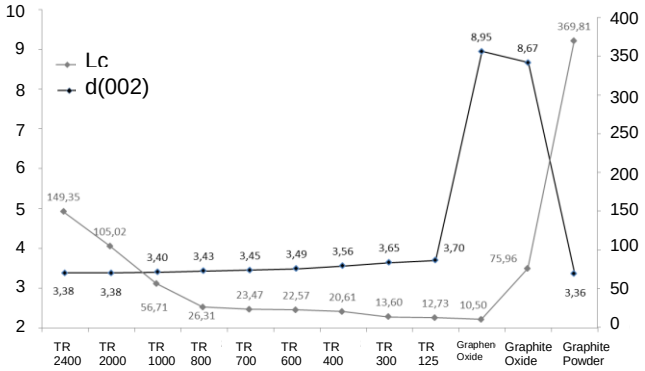

Figure 2: XRD results showing the variation of Lc and d(002) of thermally reduced graphene oxides with temperatures.

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