

On the understanding of graphene oxide structure

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Abstract

The mass-production of graphene has been one of the most important aims of the scientific community in recent years. Attempts via top-down or bottom-up methods were proposed to get an affordable graphene. There is a general agreement that top-down methods based on the chemical route, yielding graphene oxide (GO), offer a possibility for large-scale and high-production of graphene-based materials, as well as large sheet dimensions [1]. Besides the weakness of its insulating properties and the defects in its structure, it also presents the big strengths of the ease of handling of the solution process of GO, the control of the number of layers, and the capacity of tuning by chemical functionalization [2], valid for most of the high-consumption applications. Besides, partial recovery of the electrical conductivity can be achieved by chemical or thermal reduction [3]. These properties enable the use of GO and reduced GO in applications such as reinforced nanocomposites, transparent conductive films or biosensors.

The structure and chemistry of GO has been widely studied but is still uncertain. GO is a honeycomb lattice decorated with functional groups and defects but the structural models proposed are unambiguous [4], including the possibility of incorporating some self-surfactant compounds [5]. The structure of the final product depends on different factors. The nature of the starting material (crystallinity, size) [6], or synthesis procedure (intercalation and oxidant agents) have influence on the morphology and composition of GO [7].

In this work we present a study of the GO obtaining in an effort to deep into elucidating the structure. GO is obtained from two different graphitic precursors, natural graphite flakes and a carbon nanomaterial. Three different classic methods involving different oxidant agents have been compared: modified Hummers-Offeman ($\text{KMnO}_4/\text{H}_2\text{SO}_4$) [8], Brodie ($\text{HNO}_3/\text{NaClO}_3$) [9] and Staudenmaier ($\text{H}_2\text{SO}_4/\text{HNO}_3/\text{NaClO}_3$) [10]. The effectiveness of the oxidation plus exfoliation was evaluated, together with a deep characterization (XPS, NMR, Raman, HR-TEM, TG-MS) to analyze the effect of each method over each precursor in the resultant physical and chemical structure.

TEM exploration of exfoliated GO reveals noteworthy differences among the product of the abovementioned methods showing higher quality crystals for GO obtained by modified Hummers-Offeman. Multiple peak-fit for Raman Spectra helps on the understanding of the morphology and composition of GO. Deconvolutions show variations in Raman shift for each method indicating different introduction of functional groups and distinct effectiveness of the oxidation treatment. Also TG-MS signal and the quantification derived indicate variations in the mechanisms of the three oxidations.

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