

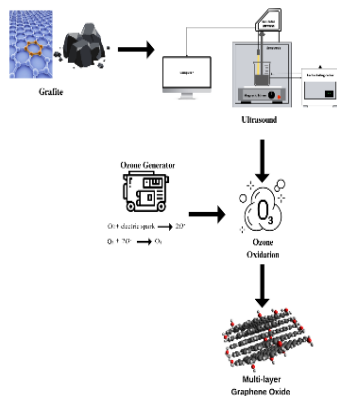
Environmentally Friendly Method to Produce Graphene Oxide from Graphite

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The role of in situ ozone oxidation in the synthesis of graphene oxide from commercial graphite was examined in this study. The materials were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Graphene oxide was obtained after an ultrasonic exfoliation process in liquid phase of the graphite layers followed by oxidation with ozone. The results demonstrated the successful synthesis of graphene oxide in multilayer form with a significant amount of oxygenated groups at the edges of the material. In this sense, the in situ ozone oxidation approach emerges as an advanced oxidative process that can significantly improve traditional methods of obtaining graphene oxide.

Introduction

The oxidation of carbon layers by the well-known Hummers method uses a mixture of strong oxidizing agents, such as H_2SO_4 and KMnO_4 , capable of forming ozone [1]. Even today it is not possible to clearly explain the reactional steps that occur during this process. What is known is that the oxidation of graphite to produce graphene oxide (GO) is explained by the presence of ozone produced during the chemical reactions [1,2].

In recent years, ozone has emerged as a potential oxidizing alternative for the synthesis of graphene oxide, as it offers a more environmentally friendly method when compared to the Hummers method, as there is no generation of by-products [3].

Ozone is known to be the most used selective oxidant when it comes to breaking carbon-carbon double bonds [3]. In particular, the direct reaction between ozone and graphite can promote the oxidation of carbon layers with the insertion of oxygenated groups mainly at the edges, which brings different functionalities to the material.

Furthermore, this oxidation can be more effective when these layers are further apart, providing space for oxygen atoms to be inserted into the structure of the material. To achieve this, mechanical exfoliation generated by ultrasonic waves is an alternative capable of separating these carbon sheets strongly united by Van der Waals forces.

Therefore, the main goal of this work is to propose an effective and sustainable methodology for the synthesis of graphene oxide through a consecutive process of mechanical exfoliation in liquid phase and oxidation by in situ ozonation of a commercial graphite.

Material and Methods

Commercial expandable graphite (CG) was purchased from Nacional de Grafite (Brazil) and ozone was generated in situ by an ozone generator (O3R, Brazil). Graphene oxide was synthesized from graphite by mechanical exfoliation in liquid phase using a probe-type ultrasonic homogenizer (Hielscher UP400St) with a coupled sonotrode (S2422D) operating at 400 W and 24 kHz. The graphite suspension in deionized water was kept in the ultrasonic probe for 2 h and the temperature was controlled by a thermostatic bath at 22 °C. Oxidation of the suspension was carried out with continuous dispersion of ozone (48 mg min^{-1}) for 18 h. Finally, the suspension was vacuum filtered using $0.22 \mu\text{m}$ PVDF membranes and the solid was dried in oven at 50 °C for 24 h. The samples were characterized by X-ray diffraction (XRD) in a Rigaku MiniFlex diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$). The X-ray generator was set at a voltage of 40 kV and a current of 40 mA. Fourier transform infrared spectroscopy (FTIR) analysis was performed on a PerkinElmer spectrophotometer using KBr pellets. The morphology of samples was analyzed by scanning electron microscopy (SEM) on a JEOL JSM-6701F electron microscope.

Results and Discussion

Figure 1 shows the FTIR spectrum for the synthesized GO and how it differs from CG in this study. The peak identified at 1090 cm^{-1} corresponds to the stretching of C-O-C bonds in ether groups, the stretching of the aromatic sp^2 C=C bonds can be identified at 1600 cm^{-1} and the peak at 2360 cm^{-1} can be assigned to the CH_2 bonds [4,5]. The stretching and bending vibration of OH groups of water molecules adsorbed on GO and CG are identified at 3430 cm^{-1} [5].

In Figure 2, a peak characteristic of the graphitic plane was identified at $2\theta = 26^\circ$, which remains present in both samples [6]. However, the intensity of this peak is significantly reduced in GO, which indicates an almost complete destruction of this structure caused by the exfoliation of carbon layers. In Figure 3(a), the morphology of CG revealed a regular material, which is organized in layers. In Figure 3(b), it can be seen how GO is also found in layers, but these appear to be more separated from each other. This behavior is expected after the graphite goes through a mechanical exfoliation process, since the shear stress produced is capable of breaking the van der Waals forces that strongly unite the carbon layers [7]. Furthermore, the ozone oxidation was able to insert oxygen atoms between these layers, causing their separation to be even greater.

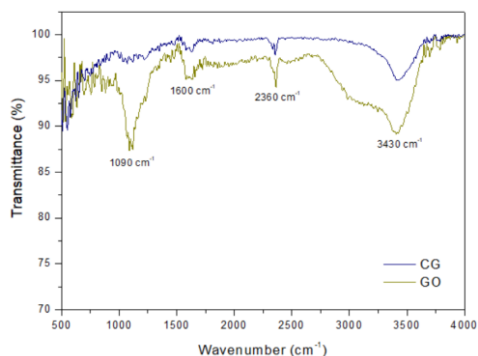


Figure 1. FTIR spectra for CG and GO.

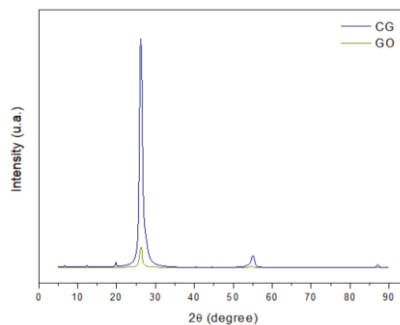


Figure 2. XRD pattern for CG and GO.

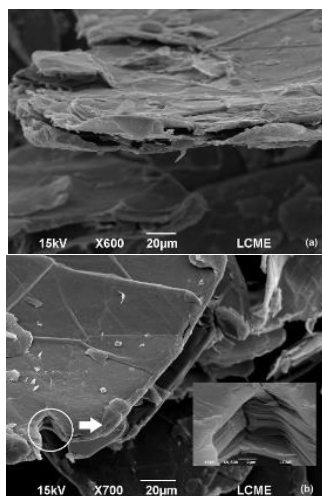


Figure 3. SEM images for (a) CG and (b) GO.

Conclusions

In this work, graphene oxide was synthesized by consecutive steps of mechanical exfoliation by ultrasonication and in situ ozonation oxidation from graphite. FTIR characterization showed that ozone plays a fundamental role in the synthesis of graphene oxide, as the insertion of oxygen functional groups into the structure of the material was identified. In XRD, a reduction in the graphitic peak was observed, which indicates a good exfoliation of the graphite layers, also confirmed by the morphological analysis, since the synthesized GO is found in a multilayer form with greater separation between them. Finally, the proposed method proved to be a more environmentally friendly alternative to the Hummers method and effective in producing graphene oxide from commercial graphite.

Acknowledgments

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