

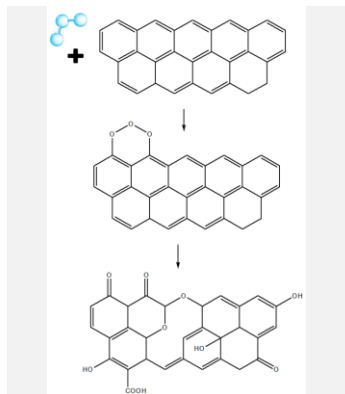
## Ozone-mediated oxidation and controlled exfoliation of graphite for the production of graphene oxide

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J. S. Salla<sup>1</sup>, R. F. P. M. Moreira<sup>1</sup>. (1) Federal University of Santa Catarina, Department of Chemical and Food Engineering, Florianópolis, Brazil, juliasallajs@gmail.com.



In this study, ozone was chosen as an oxidant for cleaving carbon-carbon double bonds in the graphitic structure and subsequent insertion of oxygenated functional groups to produce graphene oxide. The proposed method involved consecutive steps of thermal exfoliation with sulfuric acid to exfoliate the graphite layers, and increasing the distance between them. This allowed the obtaining of a graphene oxide material with fewer layers, in addition to facilitating the subsequent approximation of ozone molecules. Oxidation occurs, firstly, by physical adsorption of ozone on the surface of the material, leading to the formation of ozonide structures and the formation of oxygen functionalities, identified in the obtained graphene oxide by Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and Raman spectroscopy.

### Introduction

Ozone has found a wide range of applications as a direct oxidizing agent due to its high oxidative potential, such as effluent decontamination, food sterilization and medical therapies [1]. In addition, ozone has also been investigated to modify properties of carbonaceous materials [2]. Exposing the material to ozone allows a considerable increase in its degree of oxidation due to the insertion of functional groups containing oxygen, such as carboxylic groups, hydroxyls, ethers and carbonyls [3]. Therefore, the use of ozone as an oxidant in the synthesis of graphene oxide shows great potential for the production of graphene-based materials from graphite replacing the well-known Hummers method, that can generate large amount of gases and acidic wastewater, resulting in environmental limitations in its industrial process [4]. The liquid-phase exfoliation of graphite is considered the most promising and cost-effective method for graphene production. However, current methods often involve the use of surfactants, organic solvents, strong acids, and chemical reagents to facilitate exfoliation and stabilization in a specific medium. While surfactants improve graphene's exfoliation and stability, their use presents challenges such as toxicity and difficulty in removing residual surfactants, limiting their extensive application. The high cost and environmental impact of these reagents pose major challenges to the method. Additionally, structural damage and the introduction of impurities from chemical reagents further restrict the widespread use of the obtained graphene.

Therefore, the development of a competitive method is highly desirable due to the excellent mechanical, thermal and electrical properties of graphene-based

materials that can bring great benefits to the most diverse sectors of the economy [5].

### Material and Methods

Commercial graphite was used as raw material for the preparation of graphene oxide. Initially, 50 mL of H<sub>2</sub>SO<sub>4</sub> were added to 10 g of graphite and both were left in contact for 24 h. Thermal exfoliation was carried out in a tubular reactor inserted in a pyrolysis oven previously heated and kept at 950 °C for 30 min in N<sub>2</sub> atmosphere. The solid was dispersed in deionized water and placed in an ultrasound bath for 60 min at a frequency of 25 kHz. For the oxidative treatment, the suspension was treated with 1 L min<sup>-1</sup> of O<sub>3</sub> generated *in situ* for 16 h. Finally, the graphene oxide was separated by vacuum filtration and oven-dried at 40 °C for 12 h.

### Results and Discussion

In the FTIR spectrum presented in Figure 1 (a), peaks were identified only for graphene oxide, indicating that ozone bubbling is an effective way to oxidize graphite to graphene oxide. A key feature for ozone oxidation is the presence of peaks around 1130 and 1680 cm<sup>-1</sup>, associated with C–O–C stretching vibrations in ether groups and C=O due to carboxylic and carbonyl groups, respectively [6]. The peak identified at 2978 cm<sup>-1</sup> is related to the C–H vibrations, and the peak located at 3450 cm<sup>-1</sup> is commonly assigned to O–H in water molecule.

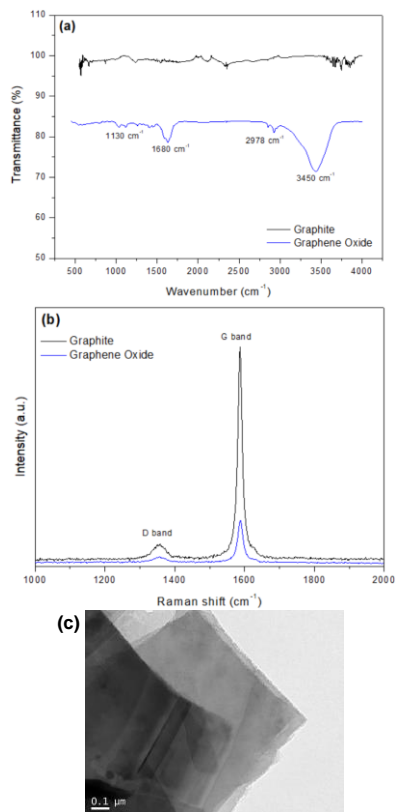
The Raman spectrum for carbon-based materials is fitted by two peaks, called D-band (1500-1600 cm<sup>-1</sup>) and G-band (1580-1600 cm<sup>-1</sup>). The D-band is related to the structural disorder of the material, originated from amorphous carbon and defects due to the presence of sp<sup>3</sup> hybridized carbons. The G-band occurs at all sp<sup>2</sup> sites and can be used as a measure

of the quality of graphene planes. The ratio between D and G bands ( $I_D/I_G$ ) is a parameter to evaluate the degree of disorder, such as defects, edges or functional groups in the graphene layers [7]. According to Figure 1 (b), the  $I_D/I_G$  ratio increased from 0.10 to 0.21 after the transformation of graphite to graphene oxide, suggesting that ozone led to a higher concentration of defects and disorder due to the number of functional group on graphene oxide structure.

Regarding the proposed method to obtain graphene oxide from graphite, the intercalation of sulfuric acid between the layers of graphite structure is necessary for the subsequent insertion of the oxidizing agent to occur. After intercalation, the material can be expanded several times over its initial volume at high temperature, resulting in separation of the graphite layers. According to Figure 1 (c), the TEM image of the obtained graphene oxide revealed a material with fewer layers. Furthermore, the use of ultrasound energy can promote greater fragmentation and disaggregation of graphite particles.

The reaction between ozone and graphite is a way of introducing oxygenated functionalities to the surface of the solid. By producing a single byproduct, oxygen, this reaction can be considered a more environmentally friendly way of oxidizing graphite into graphene oxide. At room temperature, ozone reacts with carbon after being physically adsorbed on the graphite surface. Due to the graphite low surface area, ozone adsorption is limited to the edges of graphite layers. In this way, the thermal exfoliation of graphite accompanied by the rapid evaporation of sulfuric acid, facilitates oxidation and allows ozone to reach other points of the graphene sheets beyond the edges. As oxidation first occurs via physical sorption of ozone on the graphite surface, the emergence of graphene oxide is characterized by the formation of ozonide structures,

such as 1,2,3-trioxolane [8], and, ultimately, the formation of oxygen functionalities.



**Figure 1.** FTIR (a), Raman (b) and TEM (c).

## Conclusions

In summary, in this study a method was developed for the synthesis of graphene oxide using ozone as the potential oxidizing agent aiming to insert functional groups into the layers of the material. Firstly, thermal exfoliation with sulfuric acid proved capable of separating the graphite layers, visualized by TEM images. FTIR and Raman analyzes identified the presence of oxygenated functional groups in graphene oxide, such as ethers, carboxyls and carbonyls, which were inserted onto graphene oxide layers by the physical adsorption of ozone on its surface.

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