Influence of different oxidation mechanisms on the exfoliation of intercalated graphite bisulfate using two types of graphite

Influência de diferentes mecanismos de oxidação na exfoliação de bisulfato de grafite intercalado usando dois tipos de grafite

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ABSTRACT
Three different processes for the syntheses of intercalated graphite compound have been tested in two different type of graphite, one in powder form and the other one as flakes. Each graphite was oxidized applying the same experimental conditions (sonification, neutralization, filtering and drying) but using three different auxiliary oxidizers (H2O2, HNO3 and KClO3) previously mixed with H2SO4. The resulting synthesized samples were characterized by X-ray diffraction, Raman spectroscopy and scanning electron microscopy. The Raman spectra analysis of the oxidized samples correspond to that of a graphene of few layers. Stronger delamination and exfoliation were observed in the samples of graphite, originally in powder form, treated with H2SO4/HNO3.

Keywords: graphite, graphene, Raman spectroscopy, intercalation.

RESUMO
Três processos diferentes para a sintetização de composto de grafite intercalado esfoliado foram testados em dois tipos de grafites diferentes, um em forma de pó e o outro na forma de flocos. Cada grafite foi oxidado nas mesmas condições experimentais (de sonificação, neutralização, filtragem e secagem), porém utilizando três agentes oxidantes diferentes (H2O2, HNO3 e KClO3), previamente misturados com H2SO4. As amostras sintetizadas resultantes foram caracterizadas por difração de Raios X, espectroscopia Raman e microscopia eletrônica de varredura. A análise dos espectros Raman das amostras oxidadas mostrou correspondência com a do grafeno de poucas camadas. Delaminação e exfoliação em maior proporção foram observadas nas amostras do grafite original em pó, tratado com H2SO4/HNO3.

Palavras-chaves: grafite, grafeno, espectroscopia Raman, intercalação.

1. INTRODUCTION
Materials known as Graphite Intercalation Compound (GIC) have been extensively researched in the past century as compounds that result from the insertion of ions, molecules, or atoms between the layers of the graphite, changing its crystalline structure and properties [1-5]. However, studies on graphite, GIC and the intercalation and oxidation processes has intensified even more in the last 20 years, a fact especially related to the graphite’s use as an abundant, cheap, and relatively well-known source for obtaining graphene and derivatives, as well in the search for industrial applications of these materials [6-12].

As Graphite Bisulfate Compound (GBC) are considered graphite’s layers intercalated by $H_2SO_4^-$ and $H_2SO_4$ molecules [1, 4, 13]. Different chemical reactions have been proposed as model for the synthetiza-
The reaction (1) [13] is found in the literature as one of the most used for bisulfate synthetization and it is considered the most adequate model for the reactions subject of this paper.

\[
24nC + O_{x}^{2-} + H_{2}SO_{4} \rightarrow C_{24n}^{+} \cdot HSC_{4}^{-(m-1)}H_{2}SO_{4} + HO_{x}^{(2-1)}
\]  

(1)

where \( n \) is the intercalation stage being 1, 2, 3, … the number of layers between sulfates, and \( m \) the stoichiometric factor. Each stage of intercalation \( n \) is denominated by the numbers of layers between each intercalation. Therefore, the lower \( n \), bigger is the exfoliation of the material and the possibilities for obtaining graphene.

It is important to define what is known in the scientific literature as exfoliation and intercalation, especially, of graphite. The exfoliation can be described as the shedding of the layers of a lamellar material as the graphite, resulting from a mechanical abrasion process or chemical and electrochemical methods. The intercalation is the insertion of ions, atoms, or molecules of one material in the interplanar spaces of the lamellar structure, what changes the structure and properties of the host material (stacking or stacking order, among others) but preserving its characteristic lamellar identity [2]. Generally, this phenomenon occurs at certain temperatures under specific conditions on the search for differentiated properties of the intercalated materials.

One of the biggest barriers for keeping the intercalations in GIC is the fact that the intercalation can be reversible [4]. Some authors reported this problem as re-staking or flocculation of the layers caused by the intercalation graphite layers, in dispersive or surfactant medium [15-17]. As described by [1, 13, 14, 18-21] the intercalation obeys some form and has the ability to expand with thermal treatment. In the characterization by RS and XRD of exfoliated or expanded GIC there are some patterns or fingerprints, well described in the literature, that allow the identification of the resulting material as graphene of multilayers [22].

From Novoselov’s [18] research, the intercalation of the graphite becomes more important as one of the sources for the synthetization of graphene, especially by methods using liquid chemical and electrochemical exfoliation of graphite [11, 12, 20, 23-26]. Since GIC can be used as a synthetization source for graphene and graphene oxide in liquid medium [9, 10, 24-28], the process is almost thoroughly known. Among others, GIC are useful for obtaining supercapacitors and superconductors [29-36]. The graphene oxide synthetization process and the intercalation process are many times considered as being the same process since the graphene oxide is an intercalation of functional groups that results of an oxidation process [13, 19], however, according to ABD-EIHAMID and collaborators [37], essential aspects related to these processes remain still unclear.

This paper presents the preliminary results of a research carried out in which two types of graphite have been used as a source of the intercalation and lamination of GBC for obtaining graphite bisulfate from three synthetization processes that used three different auxiliary oxidizers (H_{2}O_{2}, HNO_{3} and KClO_{3}) in the same experimental conditions, including the simultaneously performance of the oxidation and sonification stages, in order to identify which of the chosen oxidizers produces a greater exfoliation and delamination phenomena.

2. MATERIALS AND METHODS

Two different sorts of graphite (denominated in this text as A and B) were used: graphite “A” with purity 68-100% (0-30% silicon, specific weight 1.1 – 1.3 g/cm3, 28% gray, 72% carbon, mesh #140: max 5) as flakes and graphite “B” commercialized as Graphite 82140 (0-30% silicon, specific weight 0.36 g/cm3, 13% gray, 86.2% carbon, mesh #140: 1.1, #200:12.5, #325:46) as powder, are both provided by the Brazilian company Nacional de Grafite.

As chemical compounds were used Potassium Chlorate 98% from the Indian company Neon Lab Chemicals; Sulfuric Acid P.M.98%, Nitric Acid 65% and Hydrogen Peroxide 35%, all from Sigma-Aldrich Brazil.

For the experimental treatment of all the samples were used a QUIMIS magnetic stirrer with a heating system; an Elma ultrasonic bath equipment with internal tank volume of 5 L (filled with water) and frequency of 35 KHz; and a JUNG oven with an integrated system for gas flow (in this case hydrogen) and heating range up to 1200 °C;

Samples of 0.5 g of each type of graphite were oxidized in three different mixtures, using three different oxidizing reagents: H_{2}O_{2}, HNO_{3} and KClO_{3}. Each reagent was previously mixed until homogenization with H_{2}SO_{4}. The proportions used are shown in Table 1.
Table 1: Proportions of mixtures of graphite with oxidants and acids.

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>PROPORTIONS</th>
</tr>
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<tbody>
<tr>
<td>C/H$_2$O$_2$/H$_2$SO$_4$</td>
<td>0.5 g : 5 mL : 40 mL</td>
</tr>
<tr>
<td>C/HNO$_3$/H$_2$SO$_4$</td>
<td>0.5 g : 5 mL : 40 mL</td>
</tr>
<tr>
<td>C/KClO$_3$/H$_2$SO$_4$</td>
<td>0.5 g : 0.2 g : 40 mL</td>
</tr>
</tbody>
</table>

The samples for each graphite type mixed with each one of the three reagents were put in an ultrasonication bath at 37 kHz for four hours and then they were neutralized with 2.5 L of deionized water and put to decant for 24 h. Once decanted the samples were filtered using paper filter inside a Kitasato and adding water until the neutral pH was reached. Finally, the samples were placed to dry on the oven for 20 min at a temperature of 800 °C under nitrogen gas flow.

The resulting material samples were then characterized by X-ray Diffraction, using a Rigaku Miniflex II X-ray diffractometer (XRD), 15 kW, with copper tube ($\lambda = 0.1542$ nm); by Raman spectroscopy (RS) with a green laser (wavelength $\lambda = 532$ nm) in a RAMAN ALPHA 300R spectrometer model Witec, with software and diffraction grids coupled with wavelengths $\lambda = 488$ nm, $\lambda = 532$ nm and $\lambda = 633$ nm; and with a JSM - 6510 Scanning Electron Microscope (SEM), WD=13 mm, 30 kV, SS60, coupled with an Energy Dispersive X-ray Spectrometry (EDS) spectrometer, aiming to observe, respectively, if any intercalation occurred, if graphene (sheets or layers) was obtained, and if and how the material exfoliated.

3. RESULTS AND DISCUSSION

3.1 Analyze of XRD results

Figure 1 presents the diffractograms that show, in some typical regions or peaks for graphite compounds, that the intercalation seems to occur not in the same way for the different samples. The diffractogram of each pristine (original unoxidized) graphite presents a high peak (002) around the angle $2\theta \approx 26.6^\circ$ that decreased in intensity and clearly broadened in all cases after the oxidations process. This peak also shifted to lower angles as a result of the presence of defects in the crystal lattice due to the intercalation.

When H$_2$O$_2$ was used as an oxidant, in all oxidized samples the intensity of the peaks decreases and there is almost no displacement in the case of the B samples and little displacement in the case of the A samples. In both cases, that means that there was not almost any increment of basal distance, what also indicates a possible degradation of the samples or a reduction of the crystallinity. The peak becoming wider means that the crystal structure is disappearing or getting amorphous.

![Figure 1: Diffractograms of the samples of (a) graphite type A and (b) graphite type B, oxidized using H$_2$O$_2$ (blue), HNO$_3$ (red) and KClO$_3$(green); and the black discontinuous diffractogram corresponds to the pristine graphite in each case.](image)

For the B samples oxidized with HNO$_3$, the peak at $2\theta \approx 26.6^\circ$ clearly dislocates and divides itself into two peaks, the first of them appearing at $2\theta \approx 25.6^\circ$ and the second one at $2\theta \approx 26.5^\circ$. This means that an
increase of the basal distance occurred what is a clear indication of the presence of an intercalation [30]. It may have occurred the intercalation of two materials or intercalation in two differences stages. In the case of the B samples oxidized with KClO₃, the peak 2Θ ≈ 26.6° just displaces to 25.8° also indicating an increment of the basal distance and a possible intercalation.

For the A oxidized samples using HNO₃ as an oxidizing agent, in which the peak becomes wider or displaces from 2Θ ≈ 26.6° to 2Θ ≈ 26.0°. When used KClO₃ as an oxidant, the peak 2Θ ≈ 26.6° does not displace, it becomes only a little wider. Therefore, it seems that the Type A graphite exfoliated or intercalated better when HNO₃ was used as an oxidant. These results are different from Salvatore’s findings [14], that used also graphite in flakes but found better intercalation with NaClO₃. The different results described in the present work could be attributed to the characteristics of the graphite used like mesh size, purity and to some differences at experimental conditions.

3.2 Analyze of RS results

Figure 2 shows the results of the RS analysis of all oxidized samples. In that figure, the oxidizing agent used in each case is identified by the color of the spectrum (blue, red and green for H₂O₂, HNO₃ and KClO₃, respectively) and in each case, the RS of the pristine graphite is shown in black. The RS of the samples were normalized to the intensity of the G band in order to visualize better the behavior of the bands D and 2D.

In all samples, when compared with the pristine graphite, it is observed an increment of the intensity of the 2D-band (~2700 cm⁻¹) and the band becoming thinner, what indicates that the graphite degraded or exfoliated so that its structure changed to the graphene condition. According to [31, 32, 38], an intensity increase of this band indicates the reduction of the number of layers of the original graphite. Moreover, if the D-band (~1350 cm⁻¹) appears, which is typical for the deformation of graphite according to [39], and the band G (~1580 cm⁻¹) displaces a little to the right, then the material obtained is a graphene oxide or an intercalation occurred [40] and this is what the RS in Figure 2 shows for the samples oxidized with HNO₃ and KClO₃. The second order band D+D' (~2940 cm⁻¹) is also present in the spectra and this occurs specially when the obtained material is graphene or graphite whiskers are present [39].

![Figure 2: Raman spectra of the samples of (a) graphite A and (b) graphite B oxidized with H₂O₂, HNO₃ and KClO₃.](image)

3.3 Analyze of SEM results

Figures 3 and 4 contain the micrographs obtained with SEM for the comparative study of the morphology of all samples before (as pristine graphite) and after the oxidation/exfoliation treatments with the three different oxidants. In the Images the samples are identified by the letter A and B previously associated to each type of graphite accompanied by number 1, 2 or 3 referring to the oxidizing agents used (H₂O₂, HNO₃ or KClO₃, respectively). The number 0 identifies the pristine graphite in each case. The morphology of the original graphite A can be observed in the image A0 of Figure 3. It is in the form of flat flakes with mesh size much bigger than 50 µm and has a homogeneous appearance. The image or micrograph A2 corresponds to the treatment with HNO₃ as oxidizer and it shows the degradation effect and the flake layers clearly separated due to the exfoliation or delamination process that occurred.
**Figure 3:** SEM micrographs of graphite type A samples: A0 (original), oxidized with $\text{H}_2\text{O}_2$ (A1), with $\text{HNO}_3$ (A2) and with $\text{KClO}_3$ (A3).

**Figure 4:** SEM micrographs of graphite type B samples: B0 (original), oxidized with $\text{H}_2\text{O}_2$ (B1), with $\text{HNO}_3$ (B2) and with $\text{KClO}_3$ (B3).
A similar result is found with the treatment of graphite A using KClO₃ as oxidizer but to a lesser extent. The micrograph A3 of the Figure. 3 shows a strong degradation of the material and the effects of the occurred exfoliation, though, in this image the flake layers seem to be closer or have a more compact appearance if compared with image A2. The exfoliation of graphite A using HNO₃ as oxidizer is much stronger than the experimented with the two other oxidizers.

4. CONCLUSION

In this work, two different original graphite were submitted to three synthesis processes each one them characterized by the mixture used as oxidant agent H₂SO₄/H₂O₂, H₂SO₄/HNO₃ or H₂SO₄/KClO₃ but under the same experimental conditions: ultrasonic bath at 37 kHz for four hours, neutralization with 2.5 L of deionized water and decanting for 24 h, filtering in a Kitasato with paper filter and addition of water until reaching the neutral pH and drying for 20 min on oven at 800 °C under nitrogen gas flow.

Despite the morphological differences (flake or powder, mesh sizes, purity) of the two different graphite used, all samples submitted to the same treatment with each one of the three oxidizers degraded and exfoliated to a greater or lesser extent, and the resulting material is graphene of few layers. Stronger delamination and exfoliation were observed in the samples treated with H₂SO₄/HNO₃ and H₂SO₄/KClO₃ as oxidants, where multiples layers in flake form of the material visibly separate, and especially in the graphite B samples, using the originally graphite in powder form, where the relation area/volume is bigger and, therefore, the oxidant reacts with more intensity. Different from [14], in our work especially the synthesis process with the oxidizer H₂SO₄/HNO₃ lead to better results (stronger delamination and exfoliation) for both graphite types.

5. ACKNOWLEDGMENTS

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