SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE[1]

SÍNTESE E CARACTERIZAÇÃO DE ÓXIDO DE GRAFENO E ÓXIDO DE GRAFENO REDUZIDO

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ABSTRACT

Graphene oxide and reduced graphene oxide are 2D carbon materials that have been largely studied due to their unique proprieties and their potential applications. There are various methods to obtain these materials. The Hummer method is the most used, but there are several modifications that can be found in literature. In this study, two different modifications on Hummer method were tested to obtain graphene oxide and two different purification methods (filtration and centrifugation) were tested. The graphene oxides obtained were reduced. The materials were characterized by X-ray diffraction, attenuated total reflectance - Fourier transform infrared spectroscopy, Raman spectroscopy and scanning electron microscopy. According to the results obtained from the characterization techniques, the modification in Hummer method that treated the graphite before the reaction were more effective in the oxidation. This method was repeated and the results obtained were similar, what confirms that it is a method that has a good reproducibility. The results obtained from the reduction of the graphene oxides prepared were satisfactory and no difference could be noticed in the different purification methods.

Keywords: Hummer method, X-ray diffraction, scanning electron microscopy, Raman spectroscopy.

RESUMO

Óxido de grafeno e óxido de grafeno reduzido são materiais de carbono 2D que tem sido amplamente estudado devido às suas propriedades únicas e potenciais aplicações. Há diversas formas de obter esses materiais. O método de Hummer é o mais utilizado, mas várias modificações podem ser encontradas na literatura. Nesse estudo, duas diferentes modificações do método Hummer e duas formas de purificação (filtração e centrifugação) foram testadas para obtenção do óxido de grafeno. O óxido de grafeno obtido foi reduzido. Os materiais foram caracterizados por difração de raios-X, espectroscopia de infravermelho com transformada de Fourier e reflectância total atenuada, espectroscopia Raman e microscopia eletrônica de varredura. De acordo com os resultados obtidos com as técnicas de caracterização, a modificação do método de Hummer que trata o grafite antes da reação foi mais efetivo na oxidação. Esse método foi repetido e os resultados obtidos foram similares, o que confirma que é um método com boa reprodutibilidade. Os resultados obtidos para o óxido de grafeno reduzido preparados foram satisfatórios e não houve diferenças com os métodos de purificação testados.

Palavras-chave: *método de Hummer, difração de raios-X, microscopia eletrônica de varredura, espectroscopia Raman.*

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INTRODUCTION

Graphene is a 2D carbon material comprised entirely of conjugated sp^2 carbons arranged in a honeycomb structure (WANG; SALIHI; ŠILLER, 2017). Various attempts were made to synthesize graphene (SINGH et al., 2011). In 1958, Hummer and Offeman proposed a method of oxidation of graphite to improve and enhance the methods used until that date. Hummer used water free mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate. Then, he treated its final suspension with hydrogen peroxide to remove all impurities due to permanganate and manganese dioxide (HUMMERS; OFFEMAN, 1958). Quick oxidation in Hummers method was achieved because of the formation of dimanganese heptoxide. This happens because of the use of potassium permanganate, which has the strong ability to oxidize carbon atoms in graphite (SHAMAILA; SAJJAD; IQBAL, 2016).

Reduced graphene oxide is the most important among the chemically modified graphenes since its structure and properties are similar to pristine graphene and it has many applications due to its excellent electrical, mechanical and thermal properties (CHUA; PUMERA, 2014). A promising methodology is the chemical reduction of graphite oxide (STANKOVICH et al., 2006), wherein the basal plane carbon atoms are decorated with epoxide and hydroxyl groups and the edge atoms bear carbonyl and carboxyl groups (SCHNIEPP et al., 2006). The presence of these functional groups reduces the interplane forces and imparts hydrophilic character, thereby promoting complete exfoliation of single graphene oxide layers in aqueous media. Deoxygenation of graphene oxide has been accomplished by a strong chemical reducing agent, when the contained oxygen is removed (GÓMEZ-NAVARRO et al., 2007).

It has been found that proprieties of graphene oxide depend mainly on its pH behavior because pH strongly affects the hydrophilicity of graphene oxide. So, to achieve the large amount of graphene oxide and to attain their good properties, washing steps have great importance and can be done by filtration and centrifugation (SHAMAILA; SAJJAD; IQBAL, 2016).

Characterization techniques such as X-Ray diffraction and Raman spectroscopy can reveal the degree of oxidation in the final product (SHAMAILA; SAJJAD; IQBAL, 2016). Raman spectroscopy is nondestructive, fast, with high resolution and give the maximum structural and electronic information to characterize all the members of the carbon family. It is an important instrument to measure the occurrence of another carbon species in the process of making graphene and the structural damage created (FERRARI, 2007). For sp^2 nanocarbons such as graphene, Raman spectroscopy can give information about crystallite size, clustering of the sp^2 phase, the presence of sp^2-sp^3 hybridization (FERRARI; ROBERTSON, 2004).

In the present study, two different modified Hummer methods were tested to prepare graphene oxide and the effects of two techniques of purification - filtration and centrifugation - were evaluated.

The graphene oxide obtained by the two synthesis methods were reduced. The techniques X-ray diffraction, Raman spectroscopy, attenuated total reflectance - Fourier transform infrared spectroscopy and scanning electron microscopy were used to characterize the obtained materials.

MATERIALS AND METHODS

MATERIALS

For manufacturing the graphene oxide and the reduced graphene oxide, the following materials were used: graphite flakes from Aldrich, sodium nitrate P. A. and potassium permanganate P. A from Nuclear, nitric acid P. A. 65%, hydrogen peroxide and sodium chloride P. A. from Vetec, sulfuric acid P. A. and sodium citrate P. A./ A. C. S. from Synth, chloridric acid P. A. 37% from Química Moderna and sodium borohydride P. A. / A. C. S. from Neon.

GRAPHENE OXIDE PREPARATION

The graphene oxide was prepared from graphite through two different modifications in Hummer's method (HUMMERS; OFFEMAN, 1958). The first method tested were proposed by Moraes et al. (2015) with some modifications. A mixture of graphite powder (5g) and sodium nitrate (5g) was oxidized by using 200mL of 1:3 volume concentrated solution of HNO_3/H_2SO_4 maintained in an ice bath under magnetic stirring. After that, 25g of $KMnO_4$ was slowly added under vigorous stirring for 3h. Then, the solution was stirred at 60ºC for 30min and 40mL of H_2O_2 (30% vol/vol) was slowly added under magnetic stirring. Next, 50mL of HCl solution (10% vol/vol) and 450mL of cooled deionized water was slowly added and the mixture containing the graphene oxide produced was kept in a refrigerator and were named GO1.

The second method tested was published by YANG et al. (2013). Graphite powder (1g) and 60g of NaCl were mixed in a Becker glass and the mixture was grinded in a mortar until a gray powder was formed. The NaCl was added to increase the efficiency during grinding. The powder obtained was suspended in 1L of deionized water to dissolve the NaCl, and the dissolved NaCl was removed by filtration. The filter paper containing graphite powder was put into a stove at 90ºC overnight to remove the water. The remaining powder was dissolved in 98% (vol/vol) H_2SO_4 (23mL) under magnetic stirring in a three-necked flask (250mL) for 8h. The flask was placed into an ice-water bath and gradually 3g of $KMnO_4$ was added to it, leaving at least one neck open and keeping the temperature at <20ºC to avoid explosion. Then, the three-necked flask was moved into an oil bath at 40ºC under stirring. The temperature has to be precisely at 40 ± 2ºC or the quality of GO may be affected. After 30 minutes, the mixture was heated to 70ºC for 45 min. After heating for 15 min, the color of the

mixture should change to a dark brown slurry. After that, deionized water (3mL) was added to the mixture and heated to 105ºC for 5 min. Another 3mL of deionized water was added to the mixture with the temperature kept at 105ºC and after 5 min another 40 mL of deionized water was added to it with the temperature maintained at 100ºC for 15 min. Water was added slowly to make sure that the temperature is kept below 108ºC. The reaction was stopped by adding 140mL of deionized water and 10mL of H_2O_2 solution 30% (vol/vol). The mixture with the graphene oxide prepared was transferred to a 600mL Becker and to this mixture was attributed the name GO2.

GRAPHENE OXIDE PURIFICATION

The purification of graphene oxide obtained in the first method (GO1) was done by centrifugations at 2500rpm for 10min at 17ºC of the mixture five times, discarding the supernatant and washing the precipitated solid with deionized water. After the centrifugation, the graphene oxide washed was filtered and dried at 70ºC overnight. Part of it was separated for reduction of graphene oxide and another part was separated for further analysis.

Two different purification methods were tested to graphene oxide obtained by the second method (GO2). Part of GO2 was filtered, and the solid was washed with deionized water three times. The graphene oxide obtained was named GO2f and were dried at 50ºC overnight. Another part of GO2 was centrifuged at 2500rpm for 5min at room temperature. The supernatant was discarded and the precipitated solid was washed five times with deionized water. For the obtained solid, it was attributed the name GO2c. Part of both GO2f and GO2c were separated to reduce the graphene oxide and another part was separated for further analysis.

GRAPHENE OXIDE REDUCTION

The reduced graphene oxide was prepared as described by Moraes et al. (2015) with some modifications. For this preparation, for each 500mg of graphene oxide were added 50mg of sodium citrate, 200mg of sodium borohydride and 50 mL of ethanol, and the mixture was sonicated for 1h. The samples GO1, GO2f and GO2c were reduced by the same method, obtaining the reduced graphene oxides rGO1, rGO2f and rGO2c, respectively. The purification of rGO1 was done by centrifugation at 2500rpm for 10min at 17ºC. The supernatant was discharged and the precipitated solid was washed seven times with deionized water. The reduced graphene oxide obtained was dried at 50ºC overnight. The purification of rGO2f and rGO2c was done by filtration with deionized water and the solid obtained was dried at 50ºC overnight.

CHARACTERIZATION OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE

The obtained materials were characterized by X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy and the morphology of the samples were characterized by Scanning electron microscopy.

X Ray Diffraction (XRD)

The X-ray diffractograms were obtained using Bruker D2 Phaser, with CuKα radiation. The range of the measurement were from 5º to 80º, with a step of 0,05064º/s.

Raman Spectroscopy

Raman spectrum was obtained using a Renishaw in Via operating at 532nm and room temperature (25ºC) from 0 to 2500 cm^{-1}.

Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR)

Infrared spectroscopy spectrums were obtained using a Spectrum Two FT-IR Spectrometer, Perkin Elmer.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy images were obtained using a JEOL JSM-6510 series scanning electron microscope. The samples were prepared using a Denton Vacuum Desk V.

RESULTS AND DISCUSSION

X-RAY DIFFRACTION (XRD)

The X-ray diffraction was performed to evaluate the structural information of graphite used in the second method after the treatment (Figure 1), graphene oxide obtained by the different methods are shown in figure 2a (GO1, GO2c and GO2f) and reduced graphene oxides are shown in figure 2b (rGO1, rGO2f and rGO2c). This technique is useful to confirm the removal of the oxygen-containing groups after the reduction (WANG; SALIHI; ŠILLER, 2017).

There is a sharp peak at 26,5º for the pristine graphite which is in accordance to the literature (WANG; SALIHI; ŠILLER, 2017), corresponding to the Miller Indices (002). The obtained result is indexed as PDF 00-041-1487. It is possible to notice that the main peak has the intensity 497590 a.u., which indicates a high crystallinity of graphite after the treatment.

Figure 1 - X-ray diffraction of graphite.
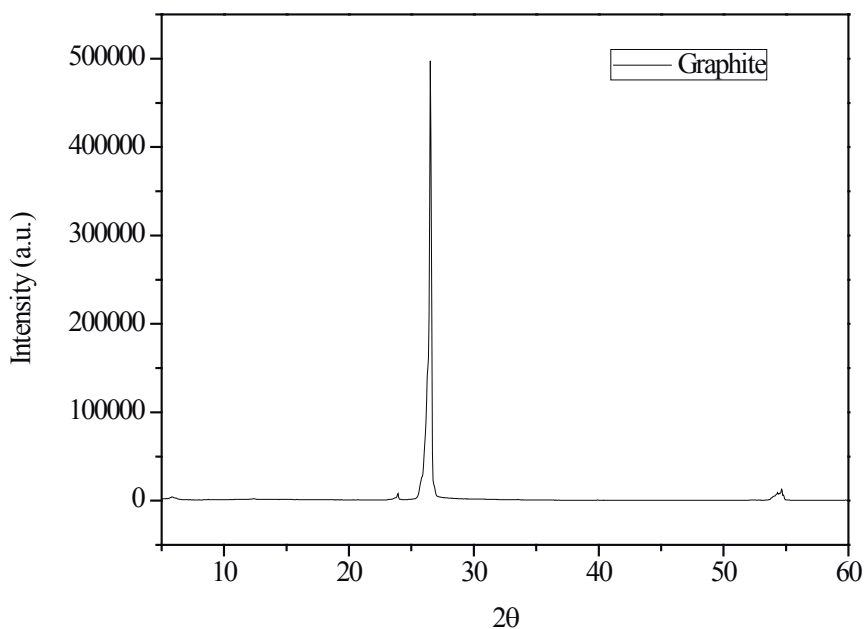
For graphene oxide, there is a diffraction peak at around 11º, which is seen in all samples, but in sample GO2f this peak is more accentuated. In this same sample, it is possible to notice that the graphite peak almost disappeared, indicating the high efficiency of the method.

For reduced graphene oxides samples, it is possible to notice the disappearance of the long-term ordering of the graphite structure. All results are in accordance with the literature (WANG; SALIHI; ŠILLER, 2017). Also, it is possible to notice that in sample GO2f the intensity of the main peak changed from 12534 a.u. to 7948 a.u. which means a reduction of 25%.

Figure 2 - X-ray diffraction of graphene oxides (a) and reduced graphene oxides (b).

(a)   (b)
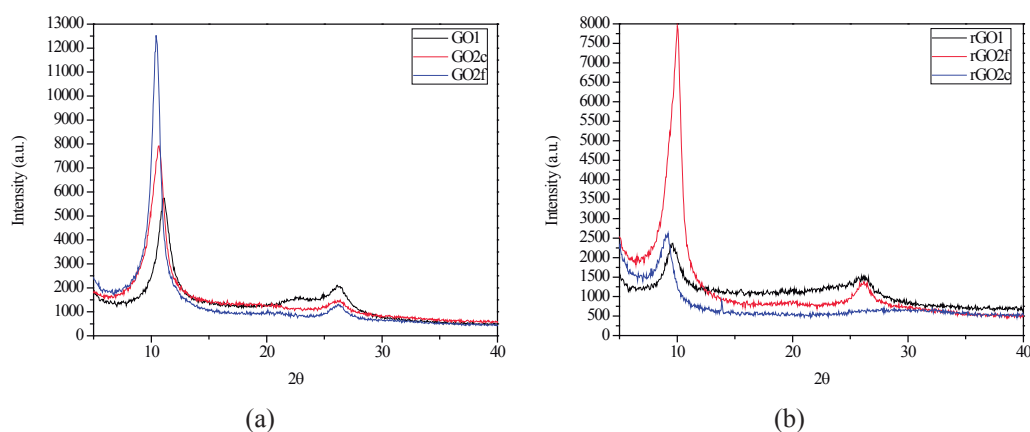
RAMAN SPECTROSCOPY

Raman spectroscopy is a powerful tool to investigate the structure and thus the intrinsic quality of nanocarbons such as carbon nanotubes and graphene (DRESSELHAUS et al., 2010). It was used in order to verify the oxidation of graphite and the reduction of graphene oxide. Raman spectrum of graphene consists in three main peaks: a D peak at ~1350 cm^{-1}, a G peak at ~1580 cm^{-1} and an intense 2D (also noted G') at ~2700 cm^{-1} (DRESSELHAUS et al., 2010; FERRARI et al., 2006). The G peak is attributed to the C-C bond from sp^2 carbons and it is common to all sp^2 carbon forms. This spectral feature has properties capable of distinguishing one carbon nanostructure from another. The G-band is highly sensitive to strain effects in sp^2 nanocarbons and can be used to probe any modification to the flat geometric structure of graphene, such as the strain induced by external forces by one graphene layer on another in few layer graphene. Carbon materials exhibit the G' band, which appears in the range 2500-2800 cm^{-1} and provides a very sensitive probe for characterizing specific sp^2 nanocarbons. The G' band can be used for differentiating between single and double-layer graphene according to their shape. The presence of a disorder in sp^2-hybridized carbon system can be characterized by the D band for the sp^3 carbons from defects. In high quality graphene, D band is absent as seen in Raman spectrum of crystalline graphene which has only the G band. When defects are formed the Raman spectrum of the disordered graphene exhibit two new sharp features: D band and G' band (DRESSELHAUS et al., 2010).

Raman spectroscopy were done to graphite, to the best method of obtaining graphene oxide (GO2f) and its reductions with both purification methods (rGO2f and rGO2c). The results are shown in figure 3, where it is possible to verify their significant structural changes. The G' band is possible to be seen at 2719,88 cm^{-1} in pristine graphite spectrum but it is not clear to other samples, so the number of layers could not be observed by this method. Another band that can be seen in pristine graphite spectrum is the G band at 1577,65 cm^{-1}. Both G and G' bands are in accordance with the literature for graphite Raman spectrum. In Raman spectrum of GO2f, the G band is broadened and shifted to 1599,16 cm^{-1}. The appearance of a prominent D band at 1355,14 cm^{-1} in spectrum from this samples indicating the reduction in size of the in-plane sp^2 domains, possibly due to the extensive oxidation (STANKOVICH et al., 2007). The Raman spectrum of the reduced graphene oxides, rGO2f and rGO2c, also contains the G band at 1592,40 cm^{-1} and the D band at 1347,76 cm^{-1}.

Figure 3 - Raman spectroscopy.
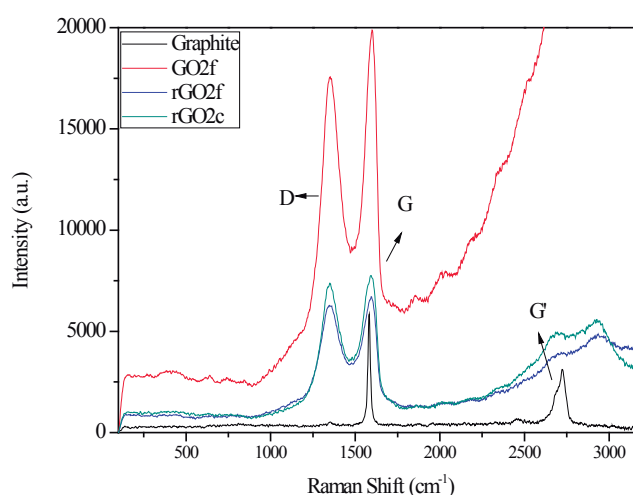
Changes in the relative intensities of the D and G bands (I_D/I_G) indicate changes in the electronic conjugation state of the graphene oxide during reduction and are useful for predicting the size of the in-plane sp^2 domain (KUDIN et al., 2007). Table 1 shows the I_D/I_G intensity ratio that increases with reduction treatment due to the restoration of the sp^2 network (WANG; SALIHI; ŠILLER, 2017).

Table 1 - Intensity of the D and G bands and I_D/I_G ratio.

	Graphite	GO2f	rGO2f	rGO2c
I_D	-	17552,7	6281,58	7369,55
I_G	5858,03	19874,79	6714,75	7753,66
I_D/I_G	-	0,88	0,93	0,951

The increase of the I_D/I_G intensity ratio suggests that smaller in-plane sp^2 domains are formed during the reduction of graphene oxide which indicates an effective reduction (BOSE et al., 2012). Besides that, the results obtained to the reductions of graphene oxides are similar, which indicates that the purification method used do not have influence in the efficiency of the reduction.

ATTENUATED TOTAL REFLECTANCE - FOURIER TRANSFORM INFRARED SPECTROSCOPY (ATR - FTIR)

ATR-FTIR analysis was used in order to evaluate the functional groups present in graphene oxide obtained by the best method (GO2f) and its reduction (rGO2f). The results are shown in figure 4.

Figure 4 - ATR-FTIR of graphene oxide and reduced graphene oxide.
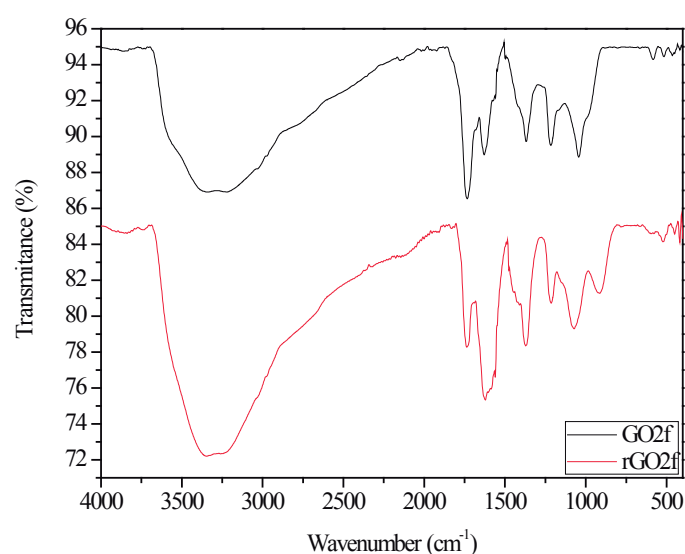
The broad absorption band at between 3000 and 3500 cm^{-1} can be attributed to OH group. Absorption bands at around 1650 cm^{-1} are observed due to carbonyl and carboxyl groups. Bands at around 400 and 950 cm^{-1} appeared due to C-O bonds of hydroxyl or epoxy groups (WANG et al., 2009). The peak around 1550 cm^{-1} is attributed to the aromatic C=C groups of the reduced graphene oxide sample (WANG; SALIHI; ŠILLER, 2017). The results are in accordance with literature and the differences between the graphene oxide and the reduced graphene oxide indicates an effective reduction.

SCANNING ELECTRON MICROSCOPY (SEM)

The morphology of graphene oxide and reduced graphene oxide obtained by the different methods were observed using scanning electron microscopy. Figure 5 shows SEM images of graphene oxide (a) obtained by the first method (GO1) where it is possible to observed its layers. The SEM image of the reduction of graphene oxide obtained by this first method is shown in figure 5b. The nature of graphene oxide can be confirmed by the typical ripples presented on their surfaces (WANG; CHEN; CHEN, 2014).
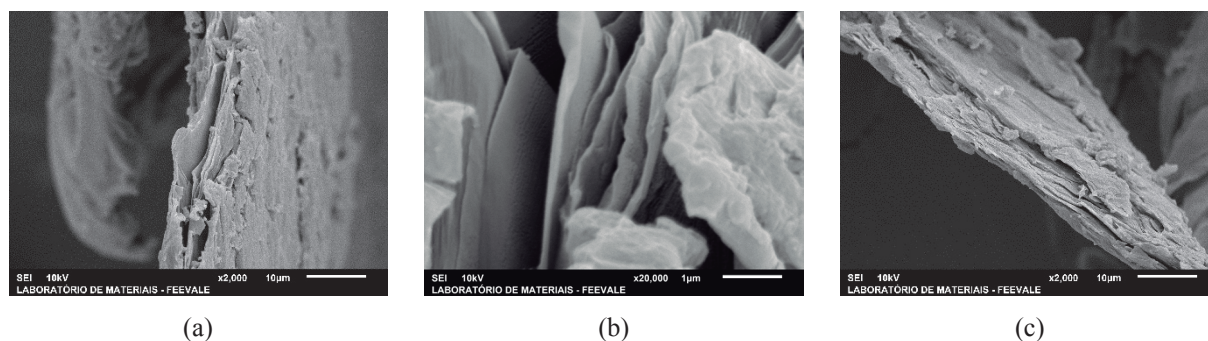
Figure 5 - SEM images of samples (a) GO1, (b) rGO1.
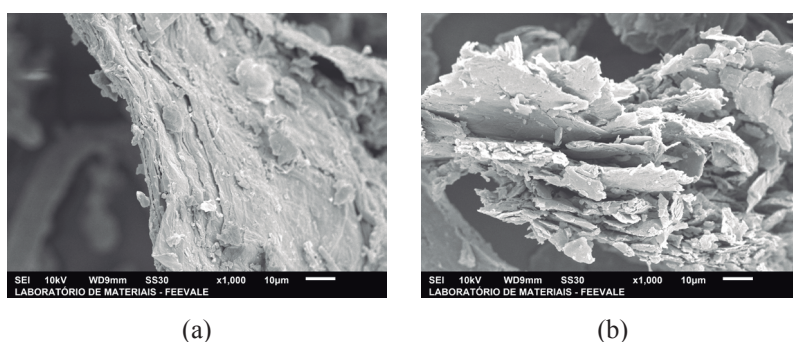
(a)   (b)

Figure 6 shows the SEM images of the graphene oxides obtained by the second method (GO2f) and its reduction (rGO2f). The layers of sample GO2f are possible to be seen in figure 6a and a close of them in figure 6b. The morphology of the reduced graphene oxide (rGO2f) can be seen in figure 6c which has a layered structure as graphene oxide, but it is possible to notice a more brittle structure.

Figure 6 - SEM images of samples (a) GO2f, (b) GO2f closer, (c) rGO2f

(a)   (b)   (c)

Besides the morphological similarities of graphene oxide and reduced graphene oxide, some differences could be seen when comparing the surface of samples GO2f (figure 7a) and rGO2f (figure 7b).

Figure 7 - SEM images of samples (a) GO2f surface and (b) rGO2f surface.

(a)   (b)
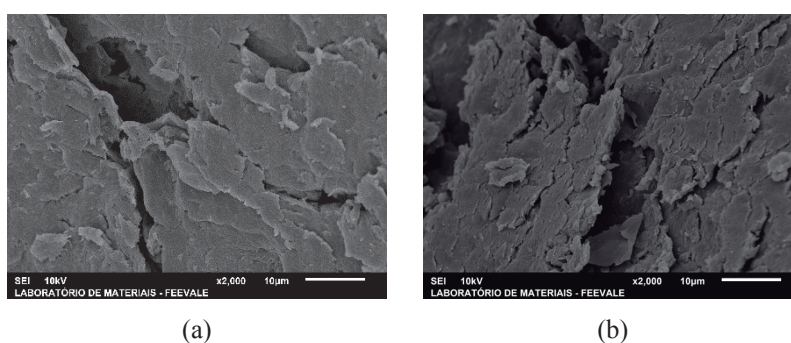
CONCLUSION

In this study, two different methods to prepare graphene oxide were tested, and both graphene oxides obtained were reduced. The samples were characterized by X-ray diffraction, Raman spectroscopy, attenuated total reflectance - Fourier transform infrared spectroscopy and scanning electron microscopy. According to the results, the second method was more efficient and could oxide more graphite than the first one. The method was repeated and the results obtained were similar, which shows that it has a good reproducibility. The graphene oxides obtained were reduced and the results obtained showed that the method was efficient.

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